

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
22 July 2004 (22.07.2004)

PCT

(10) International Publication Number  
**WO 2004/061235 A1**

(51) International Patent Classification<sup>7</sup>: **D21H 23/04**,  
17/71, 17/20, 17/37, 17/42, 17/56

(74) Agents: MANGELSEN, Christina, L. et al.; DORITY &  
MANNING, P.A., P.O. Box 1449, Greenville, SC 29602-  
1449 (US).

(21) International Application Number:  
PCT/US2003/032848

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE,  
GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,  
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK,  
MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT,  
RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR,  
TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 17 October 2003 (17.10.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
10/325,473 20 December 2002 (20.12.2002) US

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,  
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant: **KIMBERLY-CLARK WORLDWIDE,  
INC.** [US/US]; 401 N. Lake Street, Neenah, WI 54956  
(US).

(72) Inventors: **GARNIER, Gil, B., D.**; 2429 Marathon  
Avenue, Neenah, WI 54956 (US). **LINDSAY, Jeffrey, D.**;  
20 Diane Lane, Appleton, WI 54915 (US). **SHANNON,  
Thomas, G.**; 1604 Meadowbreeze Circle, Neenah, WI  
54956 (US). **LOSTOCCO, Michael, R.**; 93 Bellevue  
Place, Appleton, WI 54913 (US). **HANSEN, Lacey**; 1255  
Christopher Drive, Apartment 7, Neenah, WI 54956 (US).  
**BRANHAM, Kelly, D.**; 6661 Cross Road, Winneconne,  
WI 54986 (US). **SIDERIUS, Dan**; 6274 Woodward  
Drive, NE, Belmont, MI 49306 (US).

**Published:**

- with international search report
- before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: BICOMPONENT STRENGTHENING SYSTEM FOR PAPER

(57) Abstract: The present invention is directed to a bicomponent strengthening system and the paper webs produced with the bicomponent strengthening system. Through use of the strengthening system, paper webs may be produced in which the strength characteristics of the web may be specifically tailored. The first component of the system comprises a polymer having at least about 1.5 m-eq primary amine functionality per gram of polymer and a molecular weight of at least about 10,000 Daltons. The second component may be either a polymeric anionic compound or a polymeric aldehyde functional compound. For example, the polyamine polymer component may be a polyvinylamine or polysaccharide having primary amine functionality. In one embodiment, the second component may be a cationic polymeric aldehyde functional compound. For example, the second component may be a cationic glyoxylated polyacrylamide. In another embodiment, the second component may be a polymeric anionic compound comprising carboxy functionality.

WO 2004/061235 A1

## BICOMPONENT STRENGTHENING SYSTEM FOR PAPER

### Background of the Invention

In the art of tissue making and papermaking in general, many additives have been proposed for specific purposes, such as increasing wet strength, improving softness, or control of wetting properties. For instance, in the past, wet strength agents have been added to paper products in order to increase the strength or otherwise control the properties of the product when contacted with water and/or when used in a wet environment. For example, wet strength agents are added to paper towels so that the paper towel may be used to wipe and scrub surfaces after being wetted without the towel disintegrating. Wet strength agents are also added to facial tissues to prevent the tissues from tearing when contacting fluids. In some applications, wet strength agents are also added to bath tissues to provide strength to the tissues during use. When added to bath tissues, however, the wet strength agents should not prevent the bath tissue from disintegrating when dropped in a commode and flushed into a sewer line. Wet strength agents added to bath tissues are sometimes referred to as temporary wet strength agents since they only maintain wet strength in the tissue for a specific length of time.

Although great advancements have been made in providing strength properties to paper products, various needs still exist to increase strength properties in certain applications, as well as to allow for variability in the strength characteristics provided to a paper web by a strength agent.

In the production of permanent wet strength agents such as the series of Kymene® products from Hercules, Inc. (Wilmington, Delaware), chlorinated organic materials are commonly used. Epichlorohydrin, for example, is commonly used as a raw material, and the reaction chemistry employed typically generates other chlorinated organic materials such as 1,3-dichloro-2-propanol (DCP) and 3-chloro-1,2-propanediol (CPD). Many other wet strength materials are also chlorinated or comprise chlorine byproducts, such as the N-chlorinated polymers described in European Patent Application 289,823, published Nov. 9, 1988; or the aminopolyamide-epichlorohydrin acid salt resins of U.S. Pat. No. 5,189,142, issued Feb. 23, 1993 to Devore, et al. or U.S. Pat. No. 5,364,927, issued Nov. 15,

1994 to Devore, et al.; or the resins of U.S. Pat. No. 6,222,006, issued Apr. 24, 2001 to Kokko, et al., which are formed by reaction of an epihalohydrin and an end-capped polyaminamide polymer; or the epichlorohydrin-based resins of U.S. Pat. No. 5,644,021, issued July 1, 1997 to Maslanka.

5           Recently, interest has been growing for methods of removal of chlorinated residuals from wet-strength paper additives. Methods under consideration include, for example, using microorganisms and enzymes, as discussed at a symposium on "The Role of Biotechnology in Industrial Sustainability," May 16-17, 2002, Antwerp, Belgium. This presentation described efforts to reduce such chlorinated  
10 byproducts, including the use of bacteria capable of metabolizing such byproducts to less harmful materials. Others have sought other means to remove some of the chlorinated organic materials often found in wet strength resins. However, given the increasing environmental concerns about halogenated organic compounds, there is still a need to further reduce or eliminate the use of chlorinated  
15 compounds in wet strength resins or in the production of wet strength resins.

#### **Summary of the Invention**

The present invention is directed to a bicomponent strengthening system and a process for producing paper webs including the bicomponent strengthening system as well as the webs produced by the process. In one embodiment, the  
20 present invention is directed to a paper web in which the strength characteristics of the web may be specifically tailored through use of a bicomponent strengthening system.

In general, the process of the present invention includes providing a slurry of pulp fibers and treating the fibers with a bicomponent strengthening system  
25 prior to forming a web from the fibers. The first component of the strengthening system comprises a polymer having at least about 1.5 m-eq primary amine functionality per gram of polymer and a molecular weight of at least about 10,000 Daltons. The second component may be either a polymeric anionic compound or a polymeric aldehyde functional compound.

30           In one embodiment, the polyamine polymer may have at least about 11 m-eq primary amine functionality per gram of polymer. In another embodiment, the polyamine polymer may have at least about 15 m-eq primary amine functionality

per gram of polymer. For example, the polyamine polymer may have at least about 10 m-eq primary amine functionality and a molecular weight of about 20,000 Daltons or greater.

In one embodiment, the polyamine polymer component may be a polyvinylamine. For example, the polyamine polymer may be a polyvinylamine comprising vinylformamide units, with at least about 50% of the vinylformamide units hydrolyzed to offer amine functionality. In one embodiment, at least about 70% of the vinylformamide units may be hydrolyzed to offer amine functionality. In another embodiment, at least about 90% of the vinylformamide units may be hydrolyzed to offer amine functionality.

In another embodiment, the polyamine polymer component may be a polysaccharide having primary amine functionality.

In one embodiment, the second component may be a cationic polymeric aldehyde functional compound. For example, the second component may be a cationic glyoxylated polyacrylamide. In another embodiment, the second component may be a polymeric anionic compound comprising carboxy functionality. In one embodiment, the second component may be carboxymethyl cellulose.

Of importance, the two components are added to the pulp slurry separately, though depending on desired strength characteristics of the web, either the first or the second component may be added to the slurry before the other.

The pH of the slurry may be adjusted during the process. For example, the pH of the slurry may be adjusted to an acidic pH, such as about 6 or less in one embodiment. In another embodiment, however, the pH may be adjusted to greater than about 6.

The two components may be added to the slurry in a ratio to each other anywhere from about a 1:5 ratio to about a 5:1 ratio, as desired.

The bicomponent strengthening system of the present invention may be adjusted so as to provide either temporary or permanent wet strength to a paper web. For instance, the bicomponent strengthening system may provide temporary wet strength to a paper web such that the paper web may have less than about 70% of the initial wet tensile index remaining after soaking in water for about one

hour. In one embodiment, the paper web may have less than about 60% of the initial wet tensile index remaining after soaking in water for about one hour. For example, in one embodiment, the bicomponent strengthening system of the present invention can act as a temporary wet strength agent and the paper web  
5 thus produced may have a wet tensile index after soaking in water for about one hour of less than about 2 Nm/g.

In an alternative embodiment, the bicomponent strengthening system may provide permanent wet strength to a paper web such that the paper web may have more than about 70% of the initial wet tensile index remaining after soaking in  
10 water for about one hour. In one embodiment, the paper web may have more than about 80% of the initial wet tensile index remaining after soaking in water for about one hour.

In general, the process of the present invention includes providing a slurry of pulp fibers, sequentially adding the components of the strengthening system to  
15 the slurry of pulp fibers, depositing the slurry of pulp fibers containing the two components on a forming fabric, and drying the slurry to form a paper web.

In one embodiment, the paper web of the present invention may have a bulk greater than about 2 cc/g. For example, the paper web may have a bulk greater than about 5 cc/g.

20 The dry tensile index of the paper web can be greater than about 20 Nm/g in one embodiment. In another embodiment, the dry tensile index of the paper web can be greater than about 22 Nm/g. In yet another embodiment, the dry tensile index can be greater than about 25 Nm/g.

In general, the basis weight of the paper webs of the present invention can  
25 be any desired basis weight. For instance, in one embodiment, the paper web may have a basis weight between about 5 and about 200 gsm.

In one embodiment, the paper web of the present invention may be a multi-layer paper web, and the bicomponent strengthening system may be added to one or more layers of the web. For example, in one embodiment, a multi-layered  
30 paper web may be produced having a layer comprised primarily of soft wood fibers and a layer comprised primarily of hard wood fibers, wherein the bicomponent strengthening system is added to the layer comprised primarily of soft wood fibers.

The paper webs of the present invention may be converted and used as is to form a single ply paper product, such as a single ply bath, facial or towel product or they may be plied together, converted and used to form a multi-ply paper product, such as a multi-ply bath, facial or towel product. Any number of plies may be used.

In one embodiment, the present invention is directed to a method for decreasing the amount of low molecular weight organic chlorinated compounds in the waste stream of a paper manufacturing process. In this embodiment, the invention includes eliminating the addition of chlorinated strengthening agents to a paper manufacturing process, and replacing the chlorinated strengthening agents with the bicomponent strengthening system of the present invention. For example, in one embodiment, the bicomponent strengthening system of the present invention can replace polyamide epichlorohydrin strengthening agents in a paper manufacturing process.

#### **Definitions and Test Methods**

As used herein, a material is said to be "absorbent" if it may retain an amount of water equal to at least about 100% of its dry weight as measured by the test for Intrinsic Absorbent Capacity given below (i.e., the material has an Intrinsic Absorbent Capacity of at about 1 or greater). For example, the absorbent materials used in the absorbent members of the present invention may have an Intrinsic Absorbent Capacity of about 2 or greater, more specifically about 4 or greater, more specifically still about 7 or greater, and more specifically still about 10 or greater, with exemplary ranges of from about 3 to about 30 or from about 4 to about 25 or from about 12 to about 40.

"Papermaking fibers," as used herein, include all known cellulosic fibers or fiber mixes comprising cellulosic fibers. Fibers suitable for making the webs of this invention comprise any natural or synthetic cellulosic fibers including, but not limited to non-woody fibers, such as cotton, abaca, kenaf, sabai grass, flax, esparto grass, straw, jute hemp, bagasse, milkweed floss fibers, and pineapple leaf fibers; and woody fibers such as those obtained from deciduous and coniferous trees, including softwood fibers, such as northern and southern softwood kraft fibers; hardwood fibers, such as eucalyptus, maple, birch, and

5 aspen. Woody fibers may be prepared in high-yield or low-yield forms and may be pulped in any known method, including kraft, sulfite, high-yield pulping methods and other known pulping methods. Fibers prepared from organosolv pulping methods may also be used. A portion of the fibers, such as up to about 50% or less by dry weight, or from about 5% to about 30% by dry weight, may be synthetic fibers such as rayon, polyolefin fibers, polyester fibers, bicomponent sheath-core fibers, multi-component binder fibers, and the like. An exemplary polyethylene fiber is Pulpex®, available from Hercules, Inc. (Wilmington, DE). Any known bleaching method may be used. Synthetic cellulose fiber types include rayon in all its varieties and other fibers derived from viscose or chemically modified cellulose. Chemically treated natural cellulosic fibers may be used such as mercerized pulps, chemically stiffened or crosslinked fibers, or sulfonated fibers. For good mechanical properties in using papermaking fibers, it may be desirable that the fibers be relatively undamaged and largely unrefined or only lightly refined. While recycled fibers may be used, virgin fibers are generally useful for their mechanical properties and lack of contaminants. Mercerized fibers, regenerated cellulosic fibers, cellulose produced by microbes, rayon, and other cellulosic material or cellulosic derivatives may be used. Suitable papermaking fibers may also include recycled fibers, virgin fibers, or mixes thereof. In certain embodiments capable of high bulk and good compressive properties, the fibers may have a Canadian Standard Freeness of at least about 200, more specifically at least about 300, more specifically still at least about 400, and most specifically at least about 500.

As used herein, "high yield pulp fibers" are those papermaking fibers of pulps produced by pulping processes providing a yield of about 65 percent or greater, more specifically about 75 percent or greater, and still more specifically from about 75 to about 95 percent. Yield is the resulting amount of processed fiber expressed as a percentage of the initial wood mass. High yield pulps include bleached chemithermomechanical pulp (BCTMP), chemithermomechanical pulp (CTMP), pressure/pressure thermomechanical pulp (PTMP), thermomechanical pulp (TMP), thermomechanical chemical pulp (TMCP), high yield sulfite pulps, and high yield Kraft pulps, all of which contain fibers having high levels of lignin. Characteristic high-yield fibers may have lignin content by mass of about 1% or

greater, more specifically about 3% or greater, and still more specifically from about 2% to about 25%. Likewise, high yield fibers may have a kappa number greater than 20, for example. In one embodiment, the high-yield fibers are predominately softwood, such as northern softwood or, more specifically, northern softwood BCTMP.

As used herein, the term "cellulosic" is meant to include any material having cellulose as a major constituent, and specifically comprising about 50 percent or more by weight of cellulose or cellulose derivatives. Thus, the term includes cotton, typical wood pulps, non-woody cellulosic fibers, cellulose acetate, cellulose triacetate, rayon, viscose fibers, thermomechanical wood pulp, chemical wood pulp, debonded chemical wood pulp, lyocell and other fibers formed from solutions of cellulose in NMMO, milkweed, or bacterial cellulose. Fibers that have not been spun or regenerated from solution may be used exclusively, if desired, or at least about 80% of the web may be free of spun fibers or fibers generated from a cellulose solution.

As used herein, "bulk" and "density," unless otherwise specified, are based on an oven-dry mass of a sample and a thickness measurement made at a load of 0.34 kPa (0.05 psi) with a 7.62-cm (three-inch) diameter circular platen. Details for thickness measurements and other forms of bulk are described hereafter. As used herein, "Debonded Void Thickness" is a measure of the void volume at a microscopic level along a section of the web, which may be used to discern the differences between densified and undensified portions of the tissue or between portions that have been highly sheared and those that have been less sheared.

As used herein, the term "hydrophobic" refers to a material having a contact angle of water in air of at least 90 degrees. In contrast, as used herein, the term "hydrophilic" refers to a material having a contact angle of water in air of less than 90 degrees. As used herein, the term "surfactant" includes a single surfactant or a mixture of two or more surfactants. If a mixture of two or more surfactants is employed, the surfactants may be selected from the same or different classes, provided only that the surfactants present in the mixture are compatible with each other. In general, the surfactant may be any surfactant known to those having ordinary skill in the art, including anionic, cationic, nonionic and amphoteric



surfactants. Examples of anionic surfactants include, among others, linear and branched-chain sodium alkylbenzenesulfonates; linear and branched-chain alkyl sulfates; linear and branched-chain alkyl ethoxy sulfates; and silicone phosphate esters, silicone sulfates, and silicone carboxylates such as those manufactured by Lambent Technologies, located in Norcross, Georgia. Cationic surfactants include, by way of illustration, tallow trimethylammonium chloride and, more generally, silicone amides, silicone amido quaternary amines, and silicone imidazoline quaternary amines. Examples of nonionic surfactants, include, again by way of illustration only, alkyl polyethoxylates; polyethoxylated alkylphenols; fatty acid ethanol amides; dimethicone copolyol esters, dimethiconol esters, and dimethicone copolyols such as those manufactured by Lambent Technologies; and complex polymers of ethylene oxide, propylene oxide, and alcohols. One exemplary class of amphoteric surfactants is the silicone amphoteric manufactured by Lambent Technologies (Norcross, Georgia).

As used herein, "softening agents," sometimes referred to as "debonders," may be used to enhance the softness of the tissue product and such softening agents may be incorporated with the fibers before, during or after dispersing. Such agents may also be sprayed, printed, or coated onto the web after formation, while wet, or added to the wet end of the tissue machine prior to formation. Suitable agents include, without limitation, fatty acids, waxes, quaternary ammonium salts, dimethyl dihydrogenated tallow ammonium chloride, quaternary ammonium methyl sulfate, carboxylated polyethylene, cocamide diethanol amine, coco betaine, sodium lauryl sarcosinate, partly ethoxylated quaternary ammonium salt, distearyl dimethyl ammonium chloride, polysiloxanes and the like. Examples of suitable commercially available chemical softening agents include, without limitation, Berocell 596 and 584 (quaternary ammonium compounds) manufactured by Eka Nobel Inc., Adogen 442 (dimethyl dihydrogenated tallow ammonium chloride) manufactured by Sherex Chemical Company, Quasoft 203 (quaternary ammonium salt) manufactured by Quaker Chemical Company, and Arquad 2HT-75 ( dihydrogenated tallow) dimethyl ammonium chloride) manufactured by Akzo Chemical Company. Suitable amounts of softening agents will vary greatly with the species selected and the desired results. Such amounts may be, without limitation,

from about 0.05 to about 1 weight percent based on the weight of fiber, more specifically from about 0.25 to about 0.75 weight percent, and still more specifically about 0.5 weight percent.

Unless otherwise specified, tensile strengths are measured according to Tappi Test Method T 494 om-88 for tissue, modified in that a tensile tester is used having a 3-inch jaw width, a jaw span of 4 inches, and a crosshead speed of 10 inches per minute. Wet strength is measured in the same manner as dry strength except that the tissue sample is folded without creasing about the midline of the sample, held at the ends, and dipped in deionized water for about 0.5 seconds to a depth of about 0.5 cm to wet the central portion of the sample, whereupon the wetted region is touched for about 1 second against an absorbent towel to remove excess drops of fluid, and the sample is unfolded and set into the tensile tester jaws and immediately tested. The sample is conditioned under TAPPI conditions (50% RH, 22.7.degree. C.) before testing. Generally 5 samples are combined for wet tensile testing to ensure that the load cell reading is in an accurate range. Unless otherwise specified, the dry and wet tensile properties of machine-made webs are taken in the machine direction of the web.

Tensile index (TI) is a measure of tensile strength normalized for basis weight of the web tested in both dry and wet states. Tensile strength may be converted to tensile index by converting tensile strength determined in units of grams of force per 3 inches to units of Newtons per meter and dividing the result by the basis weight in grams per square meter of the tissue, to give the tensile index in Newton-meters per gram (Nm/g).

Wet/Dry TI Ratio (% Wet/Dry TI) is the wet TI divided by the dry TI multiplied by 100.

% Wet TI 1-hr is the ratio of wet TI remaining after 1-hr soaking versus immediate wet TI. This is a measure of wet strength permanence. For purposes of this disclosure, temporary wet strength agents are herein defined as those agents which lose more than about 30% of the wet TI after 1 hour, i.e. those strength agents wherein % wet TI 1-hr is less than about 70%.

Peak Stretch(%) is the percent elongation in the dry state at maximum load during the tensile strength test.

TEA(J/m<sup>2</sup>) is the total-energy-absorbed in the dry state at maximum load during the tensile strength test.

Elastic Modulus E(kg<sub>f</sub>) is the elastic modulus determined in the dry state and is expressed in units of kilograms of force. Tappi conditioned samples with a width of 3 inches are placed in tensile tester jaws with a gauge length (span  
5 between jaws) of 2 inches. The jaws move apart at a crosshead speed of 25.4 cm/min and the slope is taken as the least squares fit of the data between stress values of 50 grams of force and 100 grams of force, or the least squares fit of the data between stress values of 100 grams of force and 200 grams of force,  
10 whichever is greater. If the sample is too weak to sustain a stress of at least 200 grams of force without failure, an additional ply is repeatedly added until the multiply sample may withstand at least 200 grams of force without failure.

### **Brief Description of the Figures**

A full and enabling disclosure of the present invention, including the best  
15 mode thereof to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, including reference to the accompanying figure in which:

Figure 1 is a table describing physical characteristics of exemplary  
polyvinylamines suitable for the bicomponent strengthening system of the present  
20 invention.

### **Detailed Description of the Invention**

In general, the present invention is directed to a novel bicomponent  
strengthening system for a paper web that may be particularly tailored to meet the  
strengthening requirements of a paper product. More specifically, the first  
25 component of the strengthening system is a polymer containing primary amine functionality and the second component is one that may complex and/or react with the first component to form the strengthening system in a paper web.

In the process of the present invention, the first and second components  
are added separately to a slurry of pulp fibers in order to improve the strength  
30 properties of a web formed from the pulp fibers. A number of process parameters may be varied in forming the bicomponent strengthening system such that the strength characteristics of the formed paper web may be specifically tailored to

design specifications. For instance, the strength characteristics of the paper web may be varied depending on which component is added to the pulp slurry first. Strength characteristics may also be varied depending on pH of the pulp slurry, the amount of amine functionality contained on the first component, the molecular weight of the first component, the specific amine-containing polymer used, the functionality of the second component, the ionic nature of the second component, the nature of the association formed between the two components, among other possible variable parameters.

The bicomponent strengthening system of the present invention may be tailored so as to have particular dry strength characteristics as well as particular wet strength characteristics. Of particular benefit, the bicomponent strengthening system of the present invention may be tailored so as to be either a temporary wet strength agent or a permanent wet strength agent, as desired. For example in one embodiment, the bicomponent strength system may be tailored so as to function as a permanent wet strength agent, thereby rendering unnecessary the use of previously known wet strength agents. This may be particularly beneficial in those embodiments wherein the bicomponent strengthening system is used to replace wet strength agents used in the past which have been known to increase the levels of pollutants, particularly low molecular weight organic chlorinated compounds, in the effluent of paper making processes.

Various different primary amine polymers and chemical compounds may be combined in accordance with the present invention. Examples of suitable primary amine-containing polymers include various polyvinylamines, polysaccharides having primary amine functionality, and the like. Examples of suitable agents for use as the second component in the biocomponent system include polymeric anionic compounds, polymeric aldehyde functional compounds, surfactants, mixtures thereof, and the like.

Cellulosic webs prepared in accordance with the present invention may be used for a wide variety of applications. For instance, products made according to the present invention include tissue products such as facial tissues or bath tissues, paper towels, wipers, and the like. Webs made according to the present invention

may also be used in diapers, sanitary napkins, wet wipes, composite materials, molded paper products, paper cups, paper plates, and the like.

The present invention will now be discussed in greater detail. Each of the components used in the present invention will first be discussed followed by a discussion of the process used to form the bicomponent strengthening system and paper products in accordance with the present invention.

#### Polymers Having Primary Amine Functionality

The first component of the present invention may be any polymer having a suitable amount of primary amine functionality combined with a suitably high molecular weight. In particular, the first component of the strengthening system should have at least about 2 m-eq primary amine per gram of polymer. For example, the first component may have greater than about 11 m-eq primary amine per gram of polymer. In one embodiment, the first component may have at least about 15 m-eq per gram of polymer, such as about 19 m-eq primary amine per gram of polymer, or even greater amounts of amine functionality.

In addition, the first component should have a molecule weight of at least about 10,000 Daltons. For instance, in one embodiment, the first component may have a molecular weight of at least about 20,000 Daltons and at least about 10 m-eq primary amine per gram of polymer. Suitable polyamine compounds can, in certain embodiments, have a molecular weight range of about 10,000 to 1,000,000 Daltons, though polyamine compounds having any practical molecular weight range may be used. For example, polyamine polymers may have a molecular weight range of from about 5,000 to about 5,000,000, more specifically from about 20,000 to about 3,000,000, and most specifically from about 50,000 to about 500,000 may be used. For example, polyamines having molecular weights of about 50,000 to about 300,000 having molecular weights of about 40,000 to about 750,000 may be used.

Possible primary amine-containing polymers may include polyvinylamines, polyallylamines, polyethyleneimines, and the like. In one embodiment, the first component of the present invention may include polysaccharides having primary amine functionality.

In general, any suitable polyvinylamine may be used in the present invention. For instance, the polyvinylamine polymer may be a homopolymer or may be a copolymer.

Useful copolymers of polyvinylamine include those prepared by hydrolyzing polyvinylformamide to various degrees to yield copolymers of polyvinylformamide and polyvinylamine. Exemplary materials include the Catiofast® series sold commercially by BASF (Ludwigshafen, Germany). Figure 1 describes the physical characteristics of several different Catiofast® polyvinylamines which may be suitable as the first component of the bicomponent strengthening system.

The degree of hydrolysis of polyvinylamines used in the system formed by hydrolysis of polyvinylformamide, copolymer of polyvinylformamide, or derivatives thereof, may be about 10% or greater with exemplary ranges of from about 30% to about 100%, or from about 50% to about 95%. Characteristics of exemplary polyvinylamines formed by hydrolysis of polyvinylformamide are described in the table, below.

| <b>Mole %<br/>vinylamine</b> | <b>Mole %<br/>vinylformamide</b> | <b>Repeating<br/>unit Mw</b> | <b>M-eq primary<br/>amine per<br/>gram polymer</b> |
|------------------------------|----------------------------------|------------------------------|--|
| 90                           | 10                               | 45.8                         | 19.7   |
| 80                           | 20                               | 48.6                         | 16.5   |
| 70                           | 30                               | 51.4                         | 13.6   |
| 60                           | 40                               | 54.2                         | 11.1   |
| 50                           | 50                               | 57                           | 8.8  |
| 40                           | 60                               | 59.8                         | 6.7  |
| 30                           | 70                               | 62.6                         | 4.8  |
| 20                           | 80                               | 65.4                         | 3.1  |
| 10                           | 90                               | 68.2                         | 1.5  |

Polyvinylamine compounds that may be used in the present invention include copolymers of N-vinylformamide and other groups such as vinyl acetate or vinyl propionate, where at least a portion of the vinylformamide groups have been hydrolyzed. Copolymers of polyvinylamine and polyvinyl alcohol may also be utilized.

Other polymers having primary amine functionality may also be utilized. One exemplary polysaccharide having primary amine functionality that may be used in the first component of the present invention is Chitosan, which is an

amine-containing polysaccharide developed from Chitin, a naturally occurring polysaccharide extracted from recycled crab and shrimp shells. As with many of the other possible components suitable for the present invention, Chitosan will not add organic chlorinated compounds to the waste stream of a paper producing facility, and is safely biodegradable.

#### Polymeric Anionic Compounds

As stated above, according to the present invention, a polyamine polymer is sequentially combined with a second component in a pulp furnish and the bicomponent strength system may then develop. In one embodiment, the polyamine polymer may be combined with a polymeric anionic compound. When sequentially added to a pulp furnish, the polyamine and the polymeric anionic compound not only improve strength such as wet strength, but the process parameters and particular components may be tailored, offering increased control over the surface chemistry and wettability of the web formed from the pulp furnish.

In the past, polymeric anionic compounds have been used in wet strength applications. The combination of a polymeric anionic compound with a polyamine in a pulp furnish, however, has produced unexpected benefits and advantages. For instance, pulp treated with a polymeric anionic compound alone may have a slight increase in wet strength. Likewise, webs treated with a polyamine such as a polyvinylamine will also show an increase in wet strength. However, it has been discovered that sequential addition of both ingredients, a polymeric anionic compound and polyamine polymer to a pulp furnish, may result not only in enhanced wet and dry strength, but may also be tailored so as to provide specific characteristics to the paper web produced by the process. Thus, according to the present invention, it has been discovered that specific values for wet strength, dry strength, amount of wet strength remaining over a period of time (permanence of the wet strength), and the like may be varied in a paper product by varying the process parameters while employing the same or different components in the strengthening system.

This effect offers additional control over the properties of the treated web. Thus, wet and dry tensile properties may be controlled by adjusting parameters such as the relative amounts of polyamine and polymeric anionic compound, the

order of addition of the polymers to the fiber furnish, the pH of the fiber furnish, the charge ratio of the polymers, and the like.

Polymeric anionic compounds, as used herein, are polymers having repeating units containing two or more anionic functional groups that may bond to hydroxyl groups of cellulosic fibers. Such compounds may cause inter-fiber crosslinking between individual cellulose fibers. In one embodiment, the functional groups are carboxylic acids, anhydride groups, or the salts thereof. In one embodiment, the repeating units include two carboxylic acid groups on adjacent atoms, particularly adjacent carbon atoms, wherein the carboxylic acid groups are capable of forming cyclic anhydrides and specifically 5-member ring anhydrides. This cyclic anhydride, in the presence of a cellulosic hydroxyl group at elevated temperature, forms ester bonds with the hydroxyl groups of the cellulose. Polymers, including copolymers, terpolymers, block copolymers, and homopolymers, of maleic acid represent one embodiment, including copolymers of acrylic acid and maleic acid. Polyacrylic acid and associated copolymers may be useful for the present invention. In one embodiment, carboxy functionality may be added to a polymer to form the polymeric anionic compound. For example, acrylic acid functionality may be added to a glyoxylated polyacrylamide to form a suitable polymeric anionic compound. In another example, carboxymethylcellulose may be utilized. In one embodiment, the polymeric anionic compound is a poly-1,2-diacid.

Exemplary polymeric anionic compounds include the ethylene/maleic anhydride copolymers described in U.S. Patent No. 4,210,489 to Markofsky, herein incorporated by reference. Vinyl/maleic anhydride copolymers and copolymers of epichlorohydrin and maleic anhydride or phthalic anhydride are other examples. Copolymers of maleic anhydride with olefins may also be considered, including poly(styrene/maleic) anhydride. Copolymers and terpolymers of maleic anhydride may also be used. Examples of polymeric anionic compounds include terpolymers of maleic acid, vinyl acetate, and ethyl acetate known as BELCLEN@ DP80 (Durable Press 80) and BELCLEN@ DP60 (Durable Press 60), from FMC Corporation (Philadelphia, PA).

Other polymers of value may include maleic anhydride-vinyl acetate polymers, polyvinyl methyl ether-maleic anhydride copolymers, such as the



commercially available Gantrez-AN119 from International Specialty Products (Calvert City, Kentucky), isopropenyl acetate-maleic anhydride copolymers, itaconic acid-vinyl acetate copolymers, methyl styrene-maleic anhydride copolymers, styrene-maleic anhydride copolymers, methylmethacrylate-maleic anhydride copolymers, and the like.

Other terminal anionic acid groups that may be on the polymer include sulfonic acid, sulfinic acid, phosphonic acids, and the like. In addition to anhydrides, as discussed above, acid halides could be utilized, i.e. R-COX polymers where X is a halogen including fluorine, chlorine, bromine, or iodine.

The polymeric anionic compound may have any viscosity provided that the compound may be added to the pulp furnish. In some embodiments, the polymeric anionic compound may exhibit low or not solubility in water. In these particular embodiments, the polymeric anionic compound may be used in conjunction with a cosolvent or alternatively may be subjected to a period of solubilization at a high pH prior to addition to the pulp furnish.

In one embodiment, the polymeric anionic compound has a relatively low molecular weight, though polymeric anionic compounds according to the present invention may have any suitable molecular weight. For instance, in one embodiment, a carboxymethyl cellulose having a molecular weight ranging from about 70,000 Daltons to about 700,000 Daltons may be utilized. Although other molecular weight ranges are also encompassed by the second component of the strengthening system, for example, greater than about 10,000 Daltons. In one embodiment, the second component may have a molecular weight from about 10,000 Daltons to about 10,000,000 Daltons. As used herein, molecular weight refers to the weight average molecular weight determined by gel permeation chromatography (GPC) or an equivalent method.

The polymeric anionic compound may be a copolymer or terpolymer to improve flexibility of the molecule relative to the homopolymer alone. Improved flexibility of the molecule may be manifest by a reduced glass transition temperature as measured by differential scanning calorimetry.

Another useful aspect of the polymeric anionic compounds of the present invention is that relatively high pH values may be used, making the compound

more suitable for neutral and alkaline papermaking processes and more suitable for a variety of processes, machines, and fiber types. In particular, polymeric anionic compound solutions may have a pH above about 3, more specifically above about 4, more specifically still above about 6.5, and in one embodiment, 5 above about 10. In fact, paper webs including bicomponent strengthening systems formed in alkaline conditions according to the present invention may have very high wet and dry tensile indices. For example, a paper web including a polyvinylamine and a polymeric anionic compound including acrylic acid functionality bicomponent strengthening system developed at a pH of about 6.8 or 10 greater may have a dry tensile index of at least about 18 Nm/g. Moreover, when the polyvinylamine component is added to the pulp slurry before the polymeric anionic component, the dry tensile index of the product may be higher yet, in one embodiment greater than about 20 Nm/g.

In addition, the bicomponent strengthening system of the present invention 15 may provide either temporary wet strength or permanent wet strength to a web by varying the process conditions while using identical components. For example, in one embodiment, a polyvinylamine and a polymeric anionic compound including acrylic acid functionality may be sequentially added to a pulp slurry at alkaline conditions and may form a bicomponent strengthening system which may provide 20 permanent wet strength to the paper web, whereas the same components added to a pulp slurry at acidic conditions may provide temporary wet strength to the paper web.

Without wishing to be bound by theory, it is believed that a polyamine polymer containing amino groups may react in solution with the polymeric anionic 25 compound, particularly with the carboxyl groups to yield a polyelectrolyte complex (sometimes termed a coacervate) that upon heating, may react to form amide bonds that crosslink the two molecules, leaving a hydrophobic backbone. Other carboxy groups on the polymeric anionic compound may form ester cross links with hydroxyl groups on the cellulose, while amino groups on the polyamine 30 polymer may form hydrogen bonds with hydroxyl groups on the cellulose or covalent bonds with functional groups on the cellulose, such as aldehyde groups that may have been added by enzymatic or chemical treatment, or with carboxyl

groups on the cellulose that may have been provided by chemical treatment such as certain forms of bleaching or ozonation. The result is a treated web with added cross linking for wet and dry strength properties, which may also, in certain embodiments, display a high degree of hydrophobicity due to depleted hydrophilic groups on the reacted polymers.

In one embodiment, the polymeric anionic compound may be used in conjunction with a catalyst. Examples of suitable catalysts for use with polymeric anionic compounds include any catalyst that increases the rate of bond formation between the polymeric anionic compounds and cellulose fibers. Useful catalysts include alkali metal salts of phosphorous containing acids such as alkali metal hypophosphites, alkali metal phosphites, alkali metal polyphosphonates, alkali metal phosphates, and alkali metal sulfonates. Particularly desired catalysts include alkali metal polyphosphonates such as sodium hexametaphosphate, and alkali metal hypophosphites such as sodium hypophosphite. Several organic compounds are known to function effectively as catalysts as well, including imidazole (IMDZ) and triethyl amine (TEA). Inorganic compounds such as aluminum chloride and organic compounds such as hydroxyethane diphosphoric acid may also promote crosslinking.

Other specific examples of effective catalysts are disodium acid pyrophosphate, tetrasodium pyrophosphate, pentasodium tripolyphosphate, sodium trimetaphosphate, sodium tetrametaphosphate, lithium dihydrogen phosphate, sodium dihydrogen phosphate and potassium dihydrogen phosphate.

When a catalyst is used to promote bond formation, the catalyst is typically present in an amount in the range from about 5 to about 100 weight percent of the polymeric anionic compound. The catalyst is present in an amount of about 25 to about 75% by weight of the polymeric anionic compound. In one embodiment about 50% by weight of the polymeric anionic compound.

As will be described in more detail below, the polymeric anionic compound may be added to the fiber furnish sequentially with a polyamine polymer using various process techniques depending upon the particular application. For instance, one or the other of the components may be added first to the fiber

furnish, pH may be varied, relative concentrations may be varied, charge density of the polymers may be varied, and the like

In preparing a web from a fiber furnish comprising a polyamine compound and polymeric anionic compound bicomponent strengthening system, any ratio of polyamine compound mass to polymeric anionic compound mass may be used. For example, the ratio of polyamine compound to polymeric anionic compound may be from about 0.01 to about 100, more specifically from about 0.1 to about 10, more specifically still from about 0.2 to about 5, and most specifically from about 0.5 to about 1.5.

#### 10 Polymeric Aldehyde-Functional Compounds

Besides polymeric anionic compounds, another class of compounds that may be used with a polyamine in accordance with the present invention is polymeric aldehyde-functional compounds. By "aldehyde-functional " it is meant that the aldehyde groups are not bonded to other functional groups which would render them unreactive.

In one embodiment, polyamines may be combined with polymeric aldehyde-functional compounds in a papermaking furnish to create improved physical and chemical properties in the resulting web. The polyaldehyde polymer may be electronically neutral or charged, e.g., an ionic polymer such as anionic or cationic polyaldehyde polymer. Without intending to be limited or bound by theory, it is believed that the cationic polyaldehyde tends to be retained on the cellulosic fibers, which are anionic in nature. The polymeric aldehyde-functional compounds may comprise gloylated polyacrylamides, aldehyde-functional polysaccharides, and aldehyde functional cationic, anionic or non-ionic starches. Exemplary materials include those disclosed by Lovine, et al., in US Patent No. 4,129,722, herein incorporated by reference. An example of a commercially available soluble cationic aldehyde functional starch is Cobond® 1000 marketed by National Starch. The polymeric aldehyde-functional compounds may have a molecular weight of about 10,000 or greater, more specifically about 100,000 or greater, and more specifically about 500,000 or greater. Alternatively, the polymeric aldehyde-functional compounds may have a molecular weight below about 200,000, such as below about 60,000.

Further examples of aldehyde-functional polymers of use in the present invention include dialdehyde guar, aldehyde-functional wet strength additives further comprising carboxylic groups as disclosed in WO 01/83887, published November 8, 2001 by Thornton, et al., dialdehyde inulin; and the dialdehyde-modified anionic and amphoteric polyacrylamides of WO 00/11046, published March 2, 2000, the U.S. equivalent of which is application Serial No. 99/18706, filed August 19, 1998 by Geer and Staib of Hercules, Inc., herein incorporated by reference. Aldehyde-containing surfactants as disclosed in U.S. Patent No. 6,306,249 issued October 23, 2001 to Galante, et al., may also be used.

When used in the present invention, the aldehyde-functional compound may have at least about 5 m-eq of aldehyde per 100 grams of polymer, more specifically at least about 10 m-eq, more specifically still about 20 m-eq or greater, and most specifically about 25 m-eq per 100 grams of polymer or greater.

In one embodiment, the polymeric aldehyde-functional compound may be a glyoxylated polyacrylamide, such as a cationic glyoxylated polyacrylamide. Such compounds include PAREZ 631 NC wet strength resin available from Cytec Industries of West Patterson, New Jersey, and HERCOBOND 1366, manufactured by Hercules, Inc. of Wilmington, Delaware. Another example of a glyoxylated polyacrylamide is PAREZ 745, which is a glyoxylated poly(acrylamide-co-diallyl dimethyl ammonium chloride). At times it may be advantageous to utilize a mixture of high and low molecular weight glyoxylated polyacrylamides to obtain a desired effect.

The above described cationic glyoxylated polyacrylamides have been used in the past as wet strength agents. In particular, the above compounds are known as temporary wet strength additives. As used herein, a temporary wet strength agent, as opposed to a permanent wet strength agent, is defined as those resins which, when incorporated into paper or tissue products, will provide a product which retains less than about 70% of its original wet tensile index after exposure to water for a period of about one hour. Permanent wet strength agents, on the other hand, provide a product that will retain more than about 70% of its original wet tensile index after exposure to water for a period of about one hour. In accordance with the present invention, it has been discovered that when a

glyoxylated polyacrylamide, which is known to be a temporary wet strength agent, is sequentially combined with a polyamine polymer in a pulp fiber furnish, the combination of the two components may result in permanent wet strength characteristics.

5 In this manner, the wet strength characteristics of a paper product may be carefully controlled by adjusting the relative amounts of the glyoxylated polyacrylamide and the polyamine polymer as well as other process parameters, as are discussed further below.

As used herein, "wet strength agents" are materials used to immobilize the  
10 bonds between fibers in the wet state. Typically, the means by which fibers are held together in paper and tissue products involve hydrogen bonds and sometimes combinations of hydrogen bonds and covalent and/or ionic bonds. As used herein, the wet state usually will mean when the product is largely saturated with water or other aqueous solutions, but could also mean significant saturation with body  
15 fluids such as urine, blood, mucus, menses, runny bowel movement, lymph and other body exudates.

Any material that when added to a paper web or sheet results in providing the sheet with a mean wet geometric tensile strength:dry geometric tensile strength ratio in excess of about 0.1 will, for purposes of this invention, be termed  
20 a wet strength agent. As described above, typically these materials are termed either as permanent wet strength agents or as temporary wet strength agents.

In accordance with the present invention, various wet strength agents may be used in combination with a polyamine polymer. In some applications, it has been found that temporary wet strength agents combined with a polyamine  
25 polymer may result in a composition having permanent wet strength characteristics. In general, the wet strength agents that may be used in accordance with the present invention may be cationic, nonionic or anionic. In one embodiment, the additives are not strongly cationic to decrease repulsive forces in the presence of cationic polyamine.

30 Another class of compounds that may be used with a polyamine polymer in accordance with the present invention are various anionic or noncationic (e.g., zwitterionic) surfactants. Such surfactants may include, for instance, linear and

branched-chain sodium alkylbenzenesulfonates, linear and branched-chain alkyl sulfates, and linear and branched chain alkyl ethoxy sulfates. Two or more surfactants may be combined, if desired.

#### Process For Forming the Bicomponent Strengthening System

5 In one embodiment of the present invention, a polyamine polymer is added to a pulp furnish in conjunction with a second component, such as a polymeric anionic compound or a polymeric aldehyde functional compound in order to provide various benefits to the web produced from the pulp furnish. Of importance, the polyamine polymer and the second component are not mixed prior  
10 to being added to the pulp furnish, nor are they added to the pulp furnish at the same time.

After the two components have been added to the furnish, the web may be formed according to any standard web-forming process.

By way of example only, addition of either the polyamine polymer or the  
15 second component to the fiber furnish may be by either of the following methods or combination thereof:

- Direct addition to a fibrous slurry, such as by injection of the compound into a slurry prior to entry in the headbox. Slurry consistency may be from about 0.2% to about 25%, specifically from about 0.2% to about  
20 10%, more specifically from about 0.3% to about 5%, and most specifically from about 1% to about 4%.
- Addition to individualized fibers. For example, comminuted or flash dried fibers may be entrained in an air stream combined with an aerosol or spray of the compound to treat individual fibers prior to incorporation into  
25 a web or other fibrous product.

The addition level may be from about 0.5 to about 10 Kg per ton of dry fiber for either the polyamine polymer or the second component of the system. For example, in one embodiment, both components may be added to the fiber furnish at equal amounts. For example, up to about 10 kG/ton of the polyamine polymer  
30 may be added to the fiber furnish and an equal addition level of the second component may be added to the fiber furnish, i.e., up to about 10 kG/ton. Alternatively, the components may be added in different amounts. For instance,

the ratio of the polyamine to the second component added to the fiber furnish may be anywhere from about 0.01 to about 100, for example from about 0.1 to about 10, in one embodiment from about 0.2 to about 5.

5 The polyamine polymer and the second component of the system may be combined with cellulosic fibers at any pH, and in fact, this is one of the process parameters which may be adjusted so as to tailor the affect of the bicomponent strengthening system on the product web. For example, in certain embodiments, the pulp furnish may be pH adjusted to acidic levels, such as below about 6, in order to produce a bicomponent strengthening system in the web that displays  
10 temporary wet strength. In other embodiments, temporary wet strength may be produced in the web at higher pH levels with the adjustment of other process parameters, such as, for instance, the charge density of the polyamine polymer, the relative amounts of the two components, the polymer concentrations added to the furnish, the order of addition, and the like.

15 While not wishing to be bound by theory, it is believed that the nature of the association formed between the two components of the strengthening system and the cellulose fibers of the pulp furnish may depend in a large part upon the charge ratio of the bicomponent complex, which, in turn, may depend on the charge density and molecular weight of the individual components.

20 The two components of the strengthening system will be components which may form some association between each other and the pulp fibers. For example, the components may form a association wherein they are capable of bonding or otherwise associating with each other in the slurry thus forming a composition which may function in the web as a single strengthening compound, through, for  
25 example, bond formation with the fibers. Alternatively, one or both of the components may associate preferentially with the fibers and secondarily with the other component and through this reaction series, form the bicomponent strengthening system.

The term "bonding" is herein defined to include any form of chemical bond,  
30 e.g., covalent bond, electrostatic bond, coordinate bond, hydrogen bond, etc.

While the components of the strengthening system may actually form bonds with each other and/or the pulp fibers, they may alternatively associate due



to electrostatic attraction and form a polyelectrolyte complex, which may, in combination with interaction with the pulp fibers (either interaction or electrostatic interaction), form the bicomponent strengthening system of the present invention. Two mechanisms are believed possible for this type of association. In the first mechanism, the first and second components of the system form a polyelectrolyte complex in the pulp solution which may subsequently interact with the pulp fibers. The second mechanism is believed to involve formation of layers of the components on the individual pulp fibers. According to this mechanism, the component which is added first to the pulp slurry may adsorb on to the surface of the cellulose fibers (which have a strong negative charge). This first association may very likely adopt a flat configuration. The second component, once added to the slurry, may then adsorb to the fibers over the first component due to electrostatic attraction to the first component, the fiber surface, or a combination thereof. Combination of the various possible associations and interactions may also be occurring in forming the strengthening system

While at first glance, it may appear that the polyamine polymers of the system would not form a polyelectrolyte complex with cationic or neutral polymers, this is not necessarily the case. Whether or not complexation occurs can be calculated from First Principles. The classical DLVO (Derjaguin-Landau and Vervy-Overbeek) theory states that complexation may occur if the total potential of interaction between two colloids (or polymer coils) is negative. The total potential of interaction ( $V_{\text{tot}}$ ) is the sum of two main components: the electrostatic potential ( $V_{\text{el}}$ ) and the Van der Waals interactions ( $V_{\text{vw}}$ ). Thus,  $V_{\text{tot}} = V_{\text{el}} + V_{\text{vw}}$  (steric and hydrophobic potential are sometimes also included in particular applications).  $V_{\text{el}}$  may be positive (i.e. repulsive) or negative (i.e. attractive), depending on the components, and may be calculated from the Coulombic equation.  $V_{\text{vw}}$  will always be negative and may be calculated knowing the Hamaker constant. Thus, even in the case of like charges on the two components,  $V_{\text{tot}}$  may be negative and thus favor formation of a complex when the forces due to the Van der Waals interaction is greater than the force due to the electrostatic repulsion.

The examples following this description more clearly delineate some of the specific wet strength characteristics which may be obtained in the product paper webs through a variety of variations in process parameters. However, generally speaking, the primary process parameters which appear to affect the wet strength of the webs are believed to be the ionic nature of the second component, pH of the slurry at addition of the components, order of addition of the components, relative ratio of the amounts of the two components, amount of the components added to the system, and charge ratio of the components (which may depend on charge density and molecular weights of the components).

For instance, when considering a handsheet containing a bicomponent strengthening system including a polyamine polymer and a cationic second component, overall tissue strength properties may decrease with increasing pH of the system, however strength permanence may increase with increasing pH, thus a desired balance between strength permanence and overall strength of the paper web may be obtained. Furthermore, addition of a cationic component to the fiber slurry prior to addition of the polyamine polymer can improve both wet and dry strengths over those obtained with the reverse order of addition. When considering the charge density of the system, excellent overall strength benefits may be obtained from a polyamine/cationic bicomponent system wherein the two components are in about a one to one ratio, and the polyamine has a high level of charge density (greater than about 15 m-eq/gram of polymer). This particular system may also provide permanent wet strength to the paper web.

In contrast, when the second component of the strengthening system is anionic rather than cationic, not only may a paper web be produced with different overall strength characteristics, but similar variation of the process parameters can produce very different effects in the paper web. For example, when the second component of the bicomponent system is anionic, addition of the polyamine polymer to the fiber slurry prior to addition of the second component may improve overall strength characteristics of the product web, which is in contrast to the strength characteristics of a paper web containing a cationic second component. This is believed to be due to the inability of the anionic polymer to adsorb to the surface of the cellulosic fibers. Thus, when the anionic component is added first,

the two components will associate with the fibers only after the polyamine component has been added, and will probably associate with the fibers as a complex, whereas when the polyamine component is added first, it may associate with the fibers prior to the addition of the second component, and layers of the components may build up on the fiber surface. Additionally, when the second component is anionic, the best overall strength characteristics in the paper web are obtained when there is a greater amount of polyamine polymer in the system than there is of the anionic second component, e.g., when the polyamine polymer:anionic component ratio is between about 2:1 and about 5:1.

Clearly, the bicomponent strengthening system of the present invention may produce quite different strength characteristics in the paper web produced from the treated fibers depending on process parameters. This variability in the bicomponent strengthening system can provide for a strengthening system which may be tailored to obtain a combination of specific strength characteristics in a paper web. For example, a paper web may be produced with a desired dry strength, wet strength, wet strength permanence, and the like within a very narrow range through variation in the components forming the strengthening system. More particularly, in contrast to the rigid, uniform reactivity of strengthening agents used in the past, which provided limited variability in strength characteristics of the paper webs incorporating the agents, the bicomponent strengthening system of the present invention provides great variability in the reactivity of the system and may be utilized to produce paper webs with a wide variety of strength characteristics. For example, if a paper web is desired with specific set of strength characteristics, routine experimentation with the bicomponent strengthening system of the present invention can provide the particular system suitable to obtain the desired product web.

Because the bicomponent strengthening system of the present invention can be specifically tailored to provide a paper product with desired strength characteristics, it may be used in place of previously known strength agents, including, for example, strength agents which may have undesired process effects, such as those which increase the level of chlorinated organic compounds in the waste stream of the paper-making process. Through use of the present invention,

levels of these pollutants may be reduced or even eliminated from the waste stream. To reduce the chlorinated organic compounds in a waste stream of a papermaking process, one may consider any paper manufacturing process employing chlorinated strength agents, such as wet strength agents derived from epichlorohydrin. Complete or partial elimination of the chlorinated strength agents may be implemented, either suddenly or phased in over a period of time such as a day or week, with a substantially or totally organic-chlorine-free bicomponent strengthening system of the present invention being used (either suddenly introduced or phased in over a period of time) to provide at least a portion or all of the wet or dry strength that was previously contributed by one or more chlorinated strength agents.

In one embodiment, the wet or dry strength of the paper product is maintained at a level at least as great as the level prior to beginning conversion to the bicomponent strength system. In another embodiment, the wet strength of the paper is at least about 90%, at least about 95%, or at least about 98% of the previous target value prior to conversion to the bicomponent strength system. In one embodiment, previously employed chlorinated organic wet strength agents are completely eliminated from the ingredients combined in the papermaking process, with a bicomponent system of the present invention being used instead. Any papermaking process can be considered, such as a papermaking process for a machine that produces at least 1 metric tonne per day (tpd) of a wet-laid paper web having a wet:dry tensile strength ratio of at least about 0.06, more specifically at least about 0.08, and most specifically at least about 0.1. such as from 0.07 to 0.35, or from about 0.1 to about 0.4. Production rates for a machine or entire mill converted to the bicomponent strength system can be much greater, such as at least about 10 tpd, 50 tpd, 100 tpd, or 300 tpd. Without limitation, the paper web may be tissue, writing paper, linerboard, packaging paper, paper intended for impregnation with resins ("prepreg"), photocopy paper, lightweight coated paper, paperboard, cardstock, and the like. The paper may contain bleached or unbleached fibers or combinations thereof. In one embodiment, the paper fibers are substantially free of fibers bleached with molecular chlorine or chlorine dioxide. In one embodiment, the paper web produced has an ISO brightness greater than

80 or greater than 90. The basis weight of the web can be about 10 gsm or greater, more specifically about 20 gsm or greater, and most specifically about 40 gsm or greater. The concentration or absolute mass emitted per 24 hours of chlorinated organic species in an effluent stream of the production facility may be reduced by 5% or more, 10% or more, or 50% or more by converting to a bicomponent system of the present invention to reach targeted wet or dry strength levels.

The bicomponent strengthening system may be selectively associated with one of a plurality of fiber types in a web, and may be adsorbed or chemisorbed onto the surface of one or more fiber types. For example, bleached kraft fibers may have a higher affinity for the bicomponent strengthening system than synthetic fibers that may be present.

#### Preparation of Paper Webs For Use In The Present Invention

The fibrous web to be formed from the fibers treated in accordance with the present invention may be wet-laid, such as webs formed with known papermaking techniques wherein the dilute aqueous fiber slurry is disposed on a moving wire to filter out the fibers and form an embryonic web which is subsequently dewatered by combinations of units including suction boxes, wet presses, dryer units, and the like. Capillary dewatering may also be applied to remove water from the web.

Drying operations may include drum drying, through drying, steam drying such as superheated steam drying, displacement dewatering, Yankee drying, infrared drying, microwave drying, radio frequency drying in general, and impulse drying.

A moist fibrous web may also be formed by foam forming processes, wherein the treated fibers are entrained or suspended in a foam prior to dewatering, or wherein foam is applied to an embryonic web prior to dewatering or drying.

For tissue webs, both creped and uncreped methods of manufacture may be used. For either creped or uncreped methods, embryonic tissue webs may be imprinted against a deflection member prior to complete drying. Deflection members have deflection conduits between raised elements, and the web is deflected into the deflection member by an air pressure differential to create bulky

domes, while the portions of the web residing on the surface of the raised elements may be pressed against the dryer surface to create a network of pattern densified areas offering strength.

The fibrous web is generally a random plurality of papermaking fibers that can, optionally, be joined together with a binder. Any papermaking fibers, as herein defined, or mixtures thereof may be used, such as bleached fibers from a kraft or sulfite chemical pulping process. Recycled fibers may also be used, as may cotton linters or papermaking fibers comprising cotton. Both high-yield and low-yield fibers may be used. In one embodiment, the fibers may be predominantly hardwood, such as at least 50% hardwood or about 60% hardwood or greater or about 80% hardwood or greater or substantially 100% hardwood. In another embodiment, the web is predominantly softwood, such as at least about 50% softwood or at least about 80% softwood, or about 100% softwood.

For many tissue applications, high brightness may be desired. Thus the papermaking fibers or the resulting paper of the present invention may have an ISO brightness of about 60 percent or greater, more specifically about 80 percent or greater, more specifically about 85 percent or greater, more specifically from about 75 percent to about 90 percent, more specifically from about 80 percent to about 90 percent, and more specifically still from about 83 percent to about 88 percent.

The fibrous web of the present invention may be formed from a single layer or multiple layers. Both strength and softness are often achieved through layered tissues, such as stratified webs wherein at least one layer comprises softwood fibers while another layer comprises hardwood or other fiber types. Layered structures produced by any means known in the art are within the scope of the present invention. In the case of multiple layers, the layers are generally positioned in a juxtaposed or surface-to-surface relationship and all or a portion of the layers may be bound to adjacent layers. The paper web may also be formed from a plurality of separate paper webs wherein the separate paper webs may be formed from single or multiple layers.

In producing such layered structure, the bicomponent strengthening system of the present invention may be present in one or more of the layers. For

example, the bicomponent strengthening system may be present in a single layer of a multilayer web or a single ply of a multi-ply paper product. Alternatively, the bicomponent strengthening system of the present invention may be present in all of the layers of a multilayer product. In one embodiment of the present invention, the strengthening system may be present in more than one layer of the product, and may be different in each layer. For example, the same components may be added to different layers of the product, but the components may be added under different process conditions, i.e. different order of addition, different pH, different concentrations, etc. such that the affect of the strengthening system is different in different layers of the product. In an alternative embodiment, the strengthening system of the present invention may be added to more than one layer of the product, but the components of the system may vary between layers. For example, polyamine polymers similar but for different charge density may be added to different layers with identical second components added to the different layers, so as to tailor the strength characteristics of the layers. Countless variations of multi layer paper products are envisioned such that the strength characteristics of each layer of the product, and thus the strength characteristics of the product itself, may be specifically tailored.

When producing stratified webs, the webs may be made by employing a single headbox with two or more strata, or by employing two or more headboxes depositing different furnishes in series on a single forming fabric, or by employing two or more headboxes each depositing a furnish on a separate forming fabric to form an embryonic web followed by joining ("couching") the embryonic webs together to form a multi-layered web. The distinct furnishes may be differentiated by at least one of strengthening system components, consistency, fiber species (e.g., eucalyptus vs. softwood, or southern pine versus northern pine), fiber length, bleaching method (e.g., peroxide bleaching vs. chlorine dioxide bleaching), pulping method (e.g., kraft versus sulfite pulping, or BCTMP vs. kraft), degree of refining, pH, zeta potential, color, Canadian Standard Freeness (CSF), fines content, size distribution, synthetic fiber content (e.g., one layer having 10% polyolefin fibers or bicomponent fibers of denier less than 6), and the presence of additives such as fillers (e.g.,  $\text{CaCO}_3$ , talc, zeolites, mica, kaolin, plastic particles such as ground

polyethylene, and the like), starch, antimicrobial additives, odor control agents, chelating agents, chemical debonders, quaternary ammonia compounds, viscosity modifiers (e.g., CMC, polyethylene oxide, guar gum, xanthan gum, mucilage, okra extract, and the like), silicone compounds, fluorinated polymers, optical

5    brighteners, and the like. For example, in one embodiment, the strengthening system of the present invention may be added to the center layer of a three layer stratified web, which primarily contains softwood fibers, to improve the strength characteristics of the multi layer web, while the outer layers may contain primarily hard wood fibers without the addition of the strengthening system of the present  
10    invention and may provide desired softness to the multilayer product.

By way of example, useful stratified headboxes may include a four-layer Beloit (Beloit, Wisc.) Concept III headbox or a Voith Sulzer (Ravensburg, Germany) ModuleJet® headbox in multilayer mode. Principles for stratifying the web are taught by Kearney and Wells in U.S. Patent No. 4,225,382, issued Sept.  
15    30, 1980, which discloses the use of two or more layers to form ply-separable tissue. In one embodiment, a first and second layer are provided from slurry streams differing in consistency. In another embodiment, two well-bonded layers are separated by an interior barrier layer such as a film of hydrophobic fibers to enhance ply separability.

20        In one embodiment for forming a multi-layer web, an initial pulp suspension is fractionated into two or more fractions differing in fiber properties, such as mean fiber length, percentage of fines, percentage of vessel elements, and the like. In one embodiment, the complete initial pulp suspension may be treated according to the present invention prior to fractionation. In another embodiment, the pulp  
25    suspension may be fractionated first, and then one or more fractions may be treated separately according to the present invention. Fractionation may be achieved by any means known in the art, including screens, filters, centrifuges, hydrocyclones, application of ultrasonic fields, electrophoresis, passage of a suspension through spiral tubing or rotating disks, and the like. The fractionated  
30    pulp streams may be treated by combination with additives or other fibers, or adjustment of the consistency to a level suitable for paper formation, and then the streams comprising the fractionated fibers may be directed to separate portions of



a stratified headbox to produce a layered tissue product. The layered sheet may have two, three, four, or more layers. A two-layered sheet may have splits based on layer basis weights such that the lighter layer has a mass of about 5% or more of the basis weight of the overall web, or about 10% or more, about 20% or more, about 30% or more, about 40% or more, or about 50%. Exemplary weight percent splits for a three-layer web include about 20%/20%/60%; about 20%/60%/20%; about 37.5%/25%/37.5%.; about 10%/50%/40%; about 40%/20%/40%; and approximately equal splits for each layer. In one embodiment, the ratio of the basis weight of an outer layer to an inner layer may be from about 0.1 to about 5; more specifically from about 0.2 to about 3, and more specifically still from about 0.5 to about 1.5. A layered paper web according to the present invention may serve as a basesheet for a double print creping operation.

In another embodiment, tissue webs of the present invention comprise multilayered structures with one or more layers having over about 20% high yield fibers such as CTMP or BCTMP. In one embodiment, the tissue web comprises a first strength layer having cellulosic fibers and the bicomponent strengthening system of the present invention. The web further comprises a second high yield layer having at least about 20% by weight high yield fibers and optional binder material such as synthetic fibers, including thermally bondable bicomponent binder fibers, resulting in a bulky multilayered structure having good strength properties.

The slurry comprising a polyamine polymer and the second component may also be free of formaldehyde or cross-linking agents that evolve formaldehyde. In addition, the slurry comprising a polyamine polymer and the second component may be free of low molecular weight organic chlorinated compounds, as the use of the strengthening system of the present invention may render the need for previously known permanent wet strength agents which include these compounds, such as polyamide epichlorohydrin strengthening agents, unnecessary.

The bicomponent strengthening system of the present invention may be used in conjunction with any known materials and chemicals that are not antagonistic to its intended use. For example, when used in the production of fibrous materials in absorbent articles or other products, odor control agents may be present, such as odor absorbents, activated carbon fibers and particles, baby

powder, baking soda, chelating agents, zeolites, perfumes or other odor-masking agents, cyclodextrin compounds, oxidizers, and the like. The absorbent article may further comprise metalphthalocyanine material for odor control, antimicrobial properties, or other purposes. SuprabSORBENT particles, fibers, or films may be employed. For example, an absorbent fibrous mat of comminuted fibers treated with the disclosed strengthening system may be combined with superabsorbent particles to serve as an absorbent core or intake layer in a disposable absorbent article such as a diaper. A wide variety of other compounds known in the art of papermaking and tissue production may be included in the webs of the present invention.

Debonders, such as quaternary ammonium compounds with alkyl or lipid side chains, may be used to provide high wet:dry tensile strength ratios by lowering the dry strength without a correspondingly large decrease in the wet strength. Softening compounds, emollients, silicones, lotions, waxes, and oils may also have similar benefits in reducing dry strength, while providing improved tactile properties such as a soft, lubricious feel. Fillers, fluorescent whitening agents, antimicrobials, ion-exchange compounds, odor-absorbers, dyes, and the like may also be added.

Hydrophobic matter added to selected regions of the web, especially the uppermost portions of a textured web, may be valuable in providing improved dry feel in articles intended for absorbency and removal of liquids next to the skin. Webs formed of fibers treated with the bicomponent strengthening system may be further treated with waxes and emollients, typically by a topical application. Hydrophobic material may also be applied over portions of the web.

When debonders are to be applied, any debonding agent (or softener) known in the art may be utilized. The debonders may include silicone compounds, mineral oil and other oils or lubricants, quaternary ammonium compounds with alkyl side chains, or the like known in the art. Exemplary debonding agents for use herein are cationic materials such as quaternary ammonium compounds, imidazolinium compounds, and other such compounds with aliphatic, saturated or unsaturated carbon chains. The carbon chains may be unsubstituted or one or more of the chains may be substituted, e.g. with hydroxyl groups. Non-limiting

examples of quaternary ammonium debonding agents useful herein include hexamethonium bromide, tetraethylammonium bromide, lauryl trimethylammonium chloride, and dihydrogenated tallow dimethylammonium methyl sulfate.

The suitable debonders may include any number of quaternary ammonium compounds and other softeners known in the art, including but not limited to, oleylimidazolinium debonders such as C-6001 manufactured by Goldschmidt or Prosoft TQ-1003 from Hercules (Wilmington, Delaware); Berocell 596 and 584 (quaternary ammonium compounds) manufactured by Eka Nobel Inc; Adogen 442 (dimethyl dihydrogenated tallow ammonium chloride) manufactured by Cromtpon; Quasoft 203 (quaternary ammonium salt) manufactured by Quaker Chemical Company; Arquad 2HT75 (di(hydrogenated tallow) dimethyl ammonium chloride) manufactured by Akzo Chemical Company; mixtures thereof; and the like.

Other debonders may be tertiary amines and derivatives thereof; amine oxides; saturated and unsaturated fatty acids and fatty acid salts; alkenyl succinic anhydrides; alkenyl succinic acids and corresponding alkenyl succinate salts; sorbitan mono-, di- and tri-esters, including but not limited to stearate, palmitate, oleate, myristate, and behenate sorbitan esters; and particulate debonders such as clay and silicate fillers.

In one embodiment, a synergistic combination of a quaternary ammonium surfactant component and a nonionic surfactant may be used.

The debonding agent may be added at a level of at least about 0.1%, specifically at least about 0.2%, more specifically at least about 0.3%, on a dry fiber basis. Typically, the debonding agent will be added at a level of from about 0.1 to about 6%, more typically from about 0.2 to about 3%, active matter on dry fiber basis. The percentages given for the amount of debonding agent are given as an amount added to the fibers, not as an amount actually retained by the fibers.

Softening agents known in the art of tissue making may also serve as debonders or hydrophobic matter suitable for the present invention and may include but not limited to: fatty acids; waxes; quaternary ammonium salts; dimethyl dihydrogenated tallow ammonium chloride; quaternary ammonium methyl sulfate; carboxylated polyethylene; cocamide diethanol amine; coco betaine; sodium lauroyl sarcosinate; partly ethoxylated quaternary ammonium salt; distearyl

dimethyl ammonium chloride; methyl-1-oleyl amidoethyl-2-oleyl imidazolinium methylsulfate (Varisoft 3690 from Witco Corporation, now Crompton in Middlebury, CT); mixtures thereof; and the like known in the art. Topical softening agents such as functional and non-functional organo polysiloxanes may be applied to the web  
5 to improve the surface feel of the product, such polysiloxane materials being well known in the art.

The debonder may be added to the web in the furnish. However, debonder may also be added to the web after formation of the wet-laid sheet. In one embodiment, the debonder is added to the fibers with either the polyamine  
10 polymer or the second component of the system, provided that adverse reactions between the components and the debonder are avoided by suitable selection of temperatures, pH values, contact time, and the like. Additives may be applied to the wet-laid sheet heterogeneously using either a single pattern or a single means of application, or using separate patterns or means of application. Heterogeneous  
15 application of a chemical additive may be by gravure printing, spraying, or any method previously discussed.

Surfactants may also be used, being mixed with either the polyamine polymer, the second component, or added separately to the web or fibers. The surfactants may be anionic, cationic, or non-ionic, including but not limited to:  
20 tallow trimethylammonium chloride; silicone amides; silicone amido quaternary amines; silicone imidazoline quaternary amines; alkyl polyethoxylates; polyethoxylated alkylphenols; fatty acid ethanol amides; dimethicone copolyol esters; dimethiconol esters; dimethicone copolyols; mixtures thereof; and the like known in the art.

25 In one embodiment, the paper webs of the present invention may be laminated with additional plies of tissue or layers of nonwoven materials such as spunbond or meltblown webs, or other synthetic or natural materials.

The web may also be calendered, embossed, slit, rewet, moistened for use as a wet wipe, impregnated with thermoplastic material or resins, treated with  
30 hydrophobic matter, printed, apertured, perforated, converted to multiply assemblies, or converted to bath tissue, facial tissue, paper towels, wipers, absorbent articles, and the like.

The tissue products of the present invention may be converted in any known tissue product suitable for consumer use. Converting may comprise calendering, embossing, slitting, printing, addition of perfume, addition of lotion or emollients or health care additives such as menthol, stacking preferably cut sheets for placement in a carton or production of rolls of finished product, and final  
5 packaging of the product, including wrapping with a poly film with suitable graphics printed thereon, or incorporation into other product forms.

Reference now will be made to various embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way  
10 of explanation of the invention, not as a limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations may be made of this invention without departing from the scope or spirit of the invention.

### Examples

#### **15 Example 1: Control – the effect of Catiofast®, Parez®, and Kymene® on wet strength development**

##### Preparation of Pulp Slurry

To prepare a pulp slurry, 24 grams (oven-dry basis) of pulp fibers were soaked in 2 liters of deionized water for 5 minutes. The pulp slurry was  
20 disintegrated for 5 minutes in a British disintegrator. The slurry was then diluted with water to a volume of 8 liters. The strength agent was then added to the slurry. The slurry was mixed with a standard mechanical mixer at moderate shear for 10 minutes after addition of the strength agent.

##### Preparation of Handsheets

25 Handsheets were made with a basis weight of 60 gsm. During handsheet formation, the appropriate amount of fiber (0.3% consistency) slurry required to make a 60 gsm sheet was measured into a graduated cylinder. The slurry was then poured from the graduated cylinder into an 8.5-inch by 8.5-inch Valley handsheet mold (Valley Laboratory Equipment, Voith, Inc.) that had been pre-filled  
30 to the appropriate level with water. After pouring the slurry into the mold, the mold was then completely filled with water, including water used to rinse the graduated cylinder. The slurry was then agitated gently with a standard perforated mixing

plate that was inserted into the slurry and moved up and down seven times, then removed. The water was then drained from the mold through a wire assembly at the bottom of the mold that retained the fibers to form an embryonic web. The forming wire was a 90x90 mesh, stainless-steel wire cloth. The web was couched from the mold wire with two blotter papers placed on top of the web with the smooth side of the blotter contacting the web. The blotters were removed and the embryonic web was lifted with the lower blotter paper, to which it was attached. The lower blotter was separated from the other blotter, keeping the embryonic web attached to the lower blotter. The blotter was positioned with the embryonic web face up, and the blotter was placed on top of two other dry blotters. Two more dry blotters were also placed on top of the embryonic web. The stack of blotters with the embryonic web was placed in a Valley hydraulic press and pressed for one minute with 100 psi applied to the web. The pressed web was removed from the blotters and placed on a Valley steam dryer containing steam at 2.5 psig pressure and heated for 2 minutes, with the wire-side surface of the web next to the metal drying surface and a felt under tension on the opposite side of the web. Felt tension was provided by a 17.5 lbs of weight pulling downward on an end of the felt that extends beyond the edge of the curved metal dryer surface. The dried handsheet was trimmed to 7.5 inches square with a paper cutter and then weighed in a heated balance with the temperature maintained at 105°C to obtain the oven dry weight of the web. The handsheets were then subjected to dry and wet tensile testing.

Three strength agents were compared within this example: Parez® 631NC (a cationic glyoxylated polyacrylamide) manufactured by Cytec Industries; Catofast® PR 8106 (a polyvinylamine from BASF); and Kymene® 557 LX (a polyaminoamide-epichlorohydrin from Hercules Inc.). These additives were each charged to an identical furnish as 1% aqueous solutions and stirred for 10 minutes. The add-on levels investigated ranged from 0 to 10-kg/T of dry fiber. pH of the slurry was maintained neutral (6.8) in each code. No additives were used in the control sample. The results are reported below in Table 1.

**Table 1:** Control Data - Effect of Wet strength Type and Concentration on Handsheet Properties (pH=6.8)

| Code    | Polymer | Concentration (Kg/T) | Dry TI (Nm/g) | Wet TI (Nm/g) | Wet TI 1-hr (Nm/g) | %Wet TI remain after 1-hr | %Wet/ Dry TI |
|---------|---------|----------------------|---------------|---------------|--------------------|---------------------------|--------------|
| control | -       | -                    | 10.7          | 0.9           | 0.7                | 8%                        | 74%          |
| 1       | PVAm    | 2.5                  | 10.9          | 1.6           | 1.5                | 94%                       | 15%          |
| 2       | PVAm    | 5                    | 18.7          | 3.9           | 3.1                | 79%                       | 21%          |
| 3       | PVAm    | 10                   | 15.6          | 3.8           | 3.1                | 81%                       | 24%          |
| 4       | CParez® | 2.5                  | 14.3          | 1.9           | 1.2                | 63%                       | 13%          |
| 5       | CParez® | 5                    | 16.5          | 2.3           | 1.4                | 61%                       | 16%          |
| 6       | CParez® | 10                   | 22.5          | 4.1           | 2.7                | 66%                       | 18%          |
| 7       | Kymene® | 2.5                  | 14.1          | 3.4           | 3.0                | 88%                       | 24%          |
| 8       | Kymene® | 5                    | 17.5          | 5.8           | 4.7                | 81%                       | 33%          |
| 9       | Kymene® | 10                   | 20.6          | 7.9           | 6.1                | 77%                       | 38%          |

Several findings may be drawn from this data. First, for handsheets prepared with Catiofast® PR 8106, wet handsheet strength does not change as dosage level is doubled from 5 to 10 kg/T of dry fiber. This effect was not seen with Kymene® and Parez®. While not wishing to be bound by theory, this behavior may be attributed to high polymer charge which limits its adsorption capacity. Second, Parez® is the most efficient dry strength agent (Code 6), while Kymene® is the most efficient wet strength resin (Code 9) as it provides the highest wet strength and wet-over-dry strength ratio. Third, Kymene®, known as a permanent wet strength agent develops a wet strength permanency ranging from 77 to 88% (Codes 7-9); Parez®, largely regarded as a temporary wet strength resin, develops a wet strength permanency ranging from 63 to 66% (Codes 4-6). Under the conditions employed, with a wet strength permanency of 81 to 94%, Catiofast® PR 8106 has been classified as a permanent wet strength agent with initial wet strength which is similar to Parez® 631NC.

#### **Example 2: Effect of pH and order of addition on PVAm/cationic Parez bicomponent**

A slurry of pulp fibers as described in Example 1 was prepared. A bicomponent strength system was formed in the slurry which included the following compounds:

- 1% aqueous solution of CParez® 631NC (a cationic glyoxylated polyacrylamide) manufactured by Cytec Industries

- 1% aqueous solution of Catiofast® PR 8106 polyvinylamine

Polyvinylamine and CParez® were added sequentially with add-on levels constant at 10 Kg/T each. The first polymer was added to the furnish and stirred for 10 minutes. The second polymer was then added to the furnish and mixed 2 minutes. Handsheets were prepared as in Example 1 and tested. Results (average of 5 samples) are given in Table 2. No additives were used in the control. The pH of the pulp furnish was adjusted as shown below in Table 2 prior to the addition of the polymers.

10 **Table 2.** Tensile data for handsheets treated with polyvinylamine /cationic Parez. Effect of pH and order of addition. (10 Kg/T PVAm with 10 Kg/T Parez.)

| Code    | First Polymer added | pH  | Dry TI (Nm/g) | Wet TI (Nm/g) | Wet TI 1 hour (Nm/g) | % Wet TI remain after 1 hour | % Wet/Dry TI |
|---------|---------------------|-----|---------------|---------------|----------------------|------------------------------|--------------|
| Control | -                   | 6.9 | 10.65         | 0.89          | 0.66                 | 74.2%                        | 8.36%        |
| 10      | PVAm                | 6.8 | 20.79         | 5.26          | 3.98                 | 75.7%                        | 19.1%        |
| 11      | Parez 631           | 6.8 | 30.43         | 7.85          | 5.61                 | 71.5%                        | 18.4%        |
| 12      | PVAm                | 4   | 32.78         | 8.45          | 5.19                 | 61.4%                        | 15.8%        |
| 13      | Parez 631           | 4   | 35.18         | 8.93          | 5.74                 | 64.3%                        | 16.3%        |
| 14      | PVAm                | 10  | 21.13         | 3.58          | 2.67                 | 74.6%                        | 12.6%        |
| 15      | Parez 631           | 10  | 29.52         | 6.48          | 4.85                 | 74.8%                        | 16.4%        |

Several findings may be drawn from this data. First, the efficiency of the PVAm/CParez system is a function of pH; best wet and dry strengths were achieved at acidic pH (pH 4). Tissue strength properties decrease as pH of the system increases. Second, the efficiency of the PVAm/CParez system is a function of the order of polymer addition; best wet and dry strengths were achieved with CParez added first. Third, the wet strength permanency, defined as the ratio of wet strength after 1 hour soaking to that measured immediately after soaking, and the wet over dry strength ratio may both be controlled with pH and the order of polymer addition. Fourth, PVAm/CParez systems develop temporary wet strength with % Wet TI remaining after 1 hour ranging from 61% to 76% (Codes 10-15); this contrasts from the behavior of PVAm by itself (Codes 1-3, Example1)



**Example 3: Polyvinylamine/cationic Parez® bicomponent strength agents -  
effect of polymer ratio and polyvinylamine charge density**

A slurry of pulp fibers as described in Example 1 was prepared. A bicomponent strength system was formed in the slurry which included the following compounds:

- 1% aqueous solution of CParez® 631NC (a cationic glyoxylated polyacrylamide) manufactured by Cytec Industries
- 1% aqueous solution of polyvinylamine

Polyvinylamine and CParez® were added sequentially with add-on levels constant at 10 Kg/T each. CParez® was added first to the furnish and stirred for 10 minutes. The polyvinylamine was then added to the furnish and mixed 2 minutes. Three types of PVAm were used: Catofast® PR 8106 (90% amine, 21 m-eq amine/g polymer), Catofast® PR 8087 (50% amine, 11 me-q/g), and Catofast® 8104 (10% amine, 2.3 m-eq/g). The total polymer concentration added to the furnish equaled 10 kg/T of dry fiber. The weight ratio of PVAm/ CParez® was varied from 0:1, 1:5, 1:2, 1:1, 2:1, 5:1, and 1:0. pH of the slurry was maintained at neutral (6.8) in each code. Handsheets were prepared as in Example 1 and tested. Results (average of 5 samples) are given in Table 3. No additives were used in the control.

**Table 3: PVAm/ CParez® Bicomponent Strength Agents - Effect of Polymer Ratio and PVAm Charge Density on Handsheet Properties (pH=6.8, 10-kg/T polymer concentration)**

| Code    | %PVAm Charge Density | PVAm:C Parez® Ratio | Dry TI (Nm/g) | Wet TI (Nm/g) | Wet TI 1-hr (Nm/g) | %Wet TI remain after 1-hr | % Wet/Dry TI | %Peak Stretch | TEA@ Peak (J/m2) | E (kgf) |
|---------|----------------------|---------------------|---------------|---------------|--------------------|---------------------------|--------------|---------------|------------------|---------|
| control | ---                  | 0:0                 | 10.7          | 0.9           | 0.7                | 8%                        | 74%          | 0.9%          | 3.7              | 319     |
| 16      | 90%                  | 0:1                 | 22.5          | 4.0           | 2.7                | 67%                       | 18%          | 1.6%          | 15.0             | 467     |
| 17      | 90%                  | 1:5                 | 28.3          | 5.9           | 3.9                | 67%                       | 21%          | 1.8%          | 21.1             | 461     |
| 18      | 90%                  | 1:2                 | 27.9          | 5.8           | 4.5                | 77%                       | 21%          | 2.1%          | 25.1             | 429     |
| 19      | 90%                  | 1:1                 | 29.2          | 6.5           | 4.7                | 72%                       | 22%          | 1.7%          | 20.5             | 485     |
| 20      | 90%                  | 2:1                 | 23.1          | 4.5           | 3.9                | 87%                       | 19%          | 1.5%          | 14.1             | 577     |
| 21      | 90%                  | 5:1                 | 24.5          | 5.1           | 4.1                | 80%                       | 21%          | 1.5%          | 14.6             | 336     |
| 22      | 90%                  | 1:0                 | 15.6          | 3.8           | 3.1                | 82%                       | 25%          | 1.0%          | 6.3              | 374     |
| 23      | 50%                  | 0:1                 | 22.5          | 4.0           | 2.7                | 67%                       | 18%          | 1.6%          | 15.0             | 467     |
| 24      | 50%                  | 1:5                 | 22.3          | 5.0           | 3.9                | 78%                       | 22%          | 1.6%          | 14.9             | 436     |
| 25      | 50%                  | 1:2                 | 19.2          | 4.2           | 3.3                | 78%                       | 22%          | 1.3%          | 9.8              | 402     |
| 26      | 50%                  | 1:1                 | 19.7          | 4.5           | 3.2                | 71%                       | 23%          | 1.3%          | 10.8             | 428     |
| 27      | 50%                  | 2:1                 | 18.9          | 4.5           | 3.5                | 78%                       | 24%          | 1.2%          | 9.6              | 429     |
| 28      | 50%                  | 5:1                 | 16.5          | 3.4           | 2.9                | 85%                       | 21%          | 1.1%          | 7.0              | 420     |
| 29      | 50%                  | 1:0                 | 12.8          | 2.1           | 1.6                | 79%                       | 16%          | 1.0%          | 5.3              | 339     |
| 30      | 10%                  | 0:1                 | 22.5          | 4.0           | 2.7                | 67%                       | 18%          | 1.6%          | 15.0             | 467     |
| 31      | 10%                  | 1:5                 | 20.1          | 3.3           | 2.1                | 65%                       | 16%          | 1.5%          | 12.5             | 439     |
| 32      | 10%                  | 1:2                 | 18.9          | 2.5           | 1.8                | 71%                       | 13%          | 1.5%          | 12.1             | 408     |
| 33      | 10%                  | 1:1                 | 17.6          | 2.6           | 1.5                | 58%                       | 15%          | 1.2%          | 8.5              | 410     |
| 34      | 10%                  | 2:1                 | 14.8          | 1.6           | 1.1                | 69%                       | 11%          | 1.0%          | 5.7              | 375     |
| 35      | 10%                  | 5:1                 | 14.7          | 1.3           | 0.9                | 67%                       | 9%           | 1.1%          | 6.5              | 409     |
| 36      | 10%                  | 1:0                 | 13.4          | 0.8           | 0.6                | 67%                       | 6%           | 1.1%          | 5.4              | 269     |

Table 3 delineates numerous trends as a consequence of both polymer ratio and PVAm charge density. First, as the charge density (% amine) of PVAm increases, dry and wet strength increase. Second, samples containing PVAm with a 50% or 90% charge density exhibit a maximum wet strength plateau at a 1:5, 1:2, 1:1, 2:1, and 5:1 PVAm/CParez® ratio. The samples containing PVAm with a 10% charge density demonstrate a decrease in wet strength as the concentration of PVAm increases and the concentration of CParez® decreases. The wet strength of samples containing just PVAm with a 10% charge density (code 36) is equivalent to the wet strength of control samples containing no additives. Therefore, the data suggests that adding PVAm with a charge density of 10%

lends little strength benefit to handsheets. Third, wet strength permanency is greatest as PVAm concentration exceeds CParez®. However, wet strength after one hour of soaking is most permanent for the 1:1 PVAm (90% charge)/CParez® sample (code 19). Wet strength permanency ranges from 58% to 87%. Fourth, wet/dry ratio is fairly constant (18-25%) for codes containing PVAm with 50% and 90% charge density. Fifth, peak stretch, TEA, and E decrease, or remain constant, as the PVAm/CParez® ratio is increased for codes containing PVAm with 10% and 50% charge density. For codes containing PVAm with 90% charge, peak stretch and TEA have a maximum at a PVAm/CParez® ratio of 1:2 while modulus peaks at 2:1. Sixth, the PVAm/CParez® bicomponent system develops dry strength efficiently. Overall, the 1:1 PVAm (90% charge)/CParez® ratio appears as the best combination for both dry and wet strength properties.

**Example 4: Polyvinylamine/CParez® bicomponent strength agents - effect of total polymer concentration**

A slurry of pulp fibers as described in Example 1 was prepared. A bicomponent strength system was formed in the slurry which included the following compounds:

- 1% aqueous solution of CParez® 631NC (a cationic glyoxylated polyacrylamide) manufactured by Cytec Industries
- 1% aqueous solution of Catiofast® PR 8106 polyvinylamine (90% amine)

The solution of CParez® was added to the furnish first and the furnish was mixed for 10 minutes. The solution of Catiofast® PR 8106 was added to the furnish second and the furnish was mixed for 2 minutes. The PVAm/CParez® ratio added to the furnish was held constant at 1:1, while the total polymer concentration was varied, at 0, 2, 4, 6, 10, and 15-kg/T of dry fiber. pH of the slurry was maintained neutral (6.8) in each code. Handsheets were prepared as described in Example 1 and tested. The results are reported in Table 4.

Table 4 clearly shows that as polymer concentration increases, dry strength, wet strength and rigidity are enhanced. Such improvement in said properties is continuous throughout the defined breadth of polymer concentration.

**Table 4: PVAm/CParez® Bicomponent Strength Agents - Effect of Polymer Concentration on Handsheet Properties (pH=6.8, 1:1 90% charge density PVAm/CParez® ratio)**

| Code    | Polymer Conc (kg/T) | Dry TI (Nm/g) | Wet TI (Nm/g) | Wet TI 1-hr (Nm/g) | %Wet TI remain after 1-hr | % Wet/Dry TI | %Peak Stretch | TEA@ Peak (J/m <sup>2</sup> ) | E (kgf) |
|---------|---------------------|---------------|---------------|--------------------|---------------------------|--------------|---------------|-------------------------------|---------|
| control | 0                   | 10.7          | 0.9           | 0.7                | 74%                       | 8%           | 0.9%          | 3.7                           | 319     |
| 37      | 2                   | 13.5          | 1.5           | 1.0                | 69%                       | 11%          | 1.1%          | 5.8                           | 374     |
| 38      | 4                   | 18.3          | 3.0           | 2.3                | 77%                       | 17%          | 1.2%          | 9.1                           | 459     |
| 39      | 6                   | 25.6          | 5.2           | 3.7                | 72%                       | 20%          | 1.8%          | 19.1                          | 426     |
| 40      | 10                  | 29.2          | 6.5           | 4.7                | 72%                       | 22%          | 1.7%          | 20.5                          | 485     |
| 41      | 15                  | 36.9          | 7.9           | 5.8                | 73%                       | 21%          | 2.7%          | 42.2                          | 615     |

**5 Example 5: Polyvinylamine/CParez® bicomponent strength agents - effect of pH and polyvinylamine charge density**

A slurry of pulp fibers as described in Example 1 was prepared. A bicomponent strength system was formed in the slurry which included the following compounds:

- 10     ▪ 1% aqueous solution of CParez® 631NC (a cationic glyoxylated polyacrylamide) manufactured by Cytec Industries
- 1% aqueous solution of a polyvinylamine

In this example, the first polymer added to the furnish was the CParez® and then the furnish was mixed for 10 minutes. The polyvinylamine then added was  
 15 either Catiofast® PR 8106 (90% amine, 21 m-eq/g charge density), Catiofast® PR 8087 (50% amine, 11 m-eq/g charge density), or Catiofast® PR 8104 (10% amine, 2.3 m-eq/g charge density). The PVAm/CParez® ratio and the total polymer concentration added to the furnish were sustained at 1:1 and 10 kg/T of dry fiber, respectively. The furnish was mixed for 2 minutes after the polyvinylamine was  
 20 added. pH of the slurry was varied between 3.5 and 10.0. Handsheets were prepared as in Example 1 and tested. The results are reported in Table 5.

**Table 5: PVAm/CParez® Bicomponent Strength Agents - Effect of pH and PVAm Charge Density on Handsheet Properties (10-kg/T polymer concentration, 1:1 PVAm/CParez® ratio)**

| Code    | %PVAm Charge Density | pH   | Dry TI (Nm/g) | Wet TI (Nm/g) | Wet TI 1-hr (Nm/g) | %Wet TI remain after 1-hr | % Wet/Dry TI | %Peak Stretch | TEA@ Peak (J/m <sup>2</sup> ) | E (kgf) |
|---------|----------------------|------|---------------|---------------|--------------------|---------------------------|--------------|---------------|-------------------------------|---------|
| control | ---                  | 6.8  | 10.7          | 0.9           | 0.7                | 74%                       | 8%           | 0.9%          | 3.7                           | 319     |
| 42      | 90%                  | 3.5  | 26.3          | 5.4           | 3.2                | 59%                       | 21%          | 2.0%          | 21.8                          | 477     |
| 43      | 90%                  | 3.9  | 27.9          | 5.8           | 3.2                | 55%                       | 21%          | 1.8%          | 21.6                          | 519     |
| 44      | 90%                  | 7.5  | 29.2          | 6.5           | 4.7                | 72%                       | 22%          | 1.7%          | 20.5                          | 485     |
| 45      | 90%                  | 10.0 | 25.6          | 5.9           | 3.9                | 67%                       | 23%          | 1.6%          | 16.7                          | 435     |
| 46      | 50%                  | 3.5  | 27.0          | 4.8           | 3.3                | 69%                       | 18%          | 1.8%          | 19.6                          | 387     |
| 47      | 50%                  | 6.8  | 19.7          | 4.5           | 3.2                | 71%                       | 23%          | 1.3%          | 10.8                          | 428     |
| 48      | 50%                  | 10.0 | 21.9          | 4.5           | 2.7                | 60%                       | 20%          | 1.4%          | 12.4                          | 382     |
| 49      | 10%                  | 3.7  | 20.1          | 3.7           | 2.1                | 56%                       | 19%          | 1.4%          | 11.6                          | 356     |
| 50      | 10%                  | 6.8  | 17.6          | 2.6           | 1.5                | 58%                       | 15%          | 1.2%          | 8.5                           | 410     |
| 51      | 10%                  | 10.0 | 16.2          | 1.7           | 1.1                | 67%                       | 10%          | 1.1%          | 6.7                           | 365     |

5 From Table 5, at 1:1 polymer ratio, a few general statements may be made regarding the influence of pH upon furnish charge balance and subsequent wet strength properties:

i.) Acidic conditions benefit CParez®/Catiofast® PR 8104 (10% amine) systems.

10 ii.) pH does not seem to affect wet handsheet strength of CParez®/Catiofast® 8087 (50% amine) systems.

iii.) Neutral pH significantly influences strength development of CParez®/Catiofast® PR 8106 (90% amine) systems. Under acid conditions, these systems show promise as bicomponent, temporary wet strength agents.

15 **Example 6: Effect of pH and order of addition on PVAm/anionic Parez Bicomponent.**

A slurry of pulp fibers as described in Example 1 was prepared. A bicomponent strength system was formed in the slurry which included the following compounds:

- 20     ▪ 1% aqueous solution of Anionic Parez (a glyoxylated polyacrylamide with acrylic acid functionalities)

- 1% aqueous solution of Catiofast® PR 8106 polyvinylamine

For all codes, Polyvinylamine was added at 5 Kg/T and AParez was added at 2.5 Kg/T. The first polymer was stirred for 10 minutes with the furnish; the second polymer was then added and mixed 2 minutes, prior to handsheet preparation. Handsheets were then prepared as described in Example 1. After formation, handsheets were subjected to tensile testing, with results (average of 5 samples) given in Table 6. No additives were used in the control.

**Table 6.** Tensile data for handsheets treated with polyvinylamine /anionic Parez.

Effect of pH and order of addition. The level of addition is 5Kg/T for PVAm 8106 and 2.5 Kg/T for anionic Parez.

| Code    | First Polymer added | pH  | Dry TI (Nm/g) | Wet TI (Nm/g) | Wet TI 1 hour (Nm/g) | %Wet TI remain after 1 hour | % Wet/Dry TI |
|---------|---------------------|-----|---------------|---------------|----------------------|-----------------------------|--------------|
| Control | -                   | 6.9 | 10.65         | 0.89          | 0.66                 | 74.2%                       | 8.36         |
| 52      | AParez              | 6.8 | 11.65         | .89           | .72                  | 81                          | 7.7          |
| 53      | PVAm                | 6.8 | 24.2          | 5.1           | 4.1                  | 80                          | 21           |
| 54      | AParez              | 6.8 | 18.4          | 3.2           | 2.8                  | 88                          | 17           |
| 55      | PVAm                | 4   | 16.6          | 2.1           | 1.2                  | 59                          | 13           |
| 56      | AParez              | 4   | 11.7          | 1.1           | .7                   | 65                          | 9            |
| 57      | PVAm                | 10  | 21.0          | 4.0           | 3.4                  | 85                          | 19           |
| 58      | AParez              | 10  | 19.4          | 3.3           | 2.8                  | 87                          | 17           |
| 59      | PVAm                | 6.8 | 19.2          | 3.89          | -                    | -                           | 20           |
| 60      | PVAm                | 6.8 | 19.8          | 3.1           | -                    | -                           | 16           |
| 61      | PVAm                | 6.8 | 26.2          | 5.2           | -                    | -                           | 20           |

Several findings may be drawn from this data. First, the anionic Parez (AParez) does not improve tissue strength properties by itself (Code 52). This is because it does not adsorb on pulp fibers. Second, the efficiency of the PVAm/AParez system is a function of pH; best wet and dry strengths were achieved at neutral pH (pH 6.8). Third, the efficiency of the PVAm/AParez system is a function of the order of polymer addition; best wet and dry strengths were achieved with PVAm added first. The pH dependency of the system is a function of the order of polymer addition. PVAm/AParez might adsorb as a polymer complex when the non-adsorbing AParez is introduced first to the furnish, whereas, multilayers might be created by adding the adsorbing PVAm first. Third,

the wet strength permanency, defined as the ratio of wet strength after 1 hour soaking to that measured immediately after soaking, and the wet over dry strength ratio may both be controlled with pH and the order of polymer addition.

**Example 7: Effect of anionic polymer and polymer concentration in PVAm/anionic polyelectrolyte bicomponent systems.**

A slurry of pulp fibers as described in Example 1 was prepared. A bicomponent strength system was formed in the slurry which included the following compounds:

- aqueous solution of an anionic polyelectrolyte
- 1% aqueous solution of a polyvinylamine (BASF Catiofast® PR 8106)

Two types of anionic polyelectrolytes were compared: Anionic Parex (a glyoxylated polyacrylamide with acrylic acid functionalities) and a low molecular weight (200,000) high charge poly (acrylamide-co-acrylic acid) (20 wt% acrylamide). BASF Catiofast® PR 8106 polyvinylamine was used in conjunction with the anionic polyelectrolyte in all instances (PVAm). For all codes, Polyvinylamine was added first as a 1% solution and stirred for 10 minutes with the furnish; the anionic polymer was then added at various concentrations and mixed 2 minutes, prior to handsheet preparation as described in Example 1. After formation, handsheets were subjected to tensile testing, with results (average of 5 samples) given in Table 7.

**Table 7.** Tensile data for handsheets treated with polyvinylamine /anionic Parez and polyvinylamine/polyacrylic acid (PAA). Effect of type of anionic polymer (PAA or AParez) and polymer concentration. PVAm added first, pH =6.8.

| Code    | PVAm concentration (Kg/T) | Anionic polymer | Anionic polymer concentration (Kg/T) | Dry TI (Nm/g) | Wet TI (Nm/g) | % Wet/Dry TI |
|---------|---------------------------|-----------------|--------------------------------------|---------------|---------------|--------------|
| Control | -                         | -               |                                      | 10.65         | 0.89          | 8.36         |
| 62      | 5                         | PAA             | 2.5                                  | 19.2          | 3.89          | 20           |
| 63      | 5                         | PAA             | 5                                    | 19.8          | 3.1           | 16           |
| 64      | 5                         | PAA             | 10                                   | 26.2          | 5.2           | 20           |
| 65      | 5                         | AParez          | 2.5                                  | 26.3          | 5.2           | 20           |
| 66      | 5                         | AParez          | 5                                    | 21.8          | 4.9           | 22           |
| 67      | 5                         | AParez          | 10                                   | 19.7          | 4.2           | 21           |
| 68      | 2.5                       | AParez          | 2.5                                  | 17.4          | 2.9           | 17           |
| 69      | 2.5                       | AParez          | 5                                    | 18.7          | 3.7           | 20           |
| 70      | 2.5                       | AParez          | 10                                   | 18            | 3.4           | 19           |

5

Several findings may be drawn from this data. First, for PVAm/PAA systems at neutral pH, handsheet wet strength and dry strength both increase as increases the concentration of PAA (codes 62, 63 and 64). Code 64 has similar properties to code 65, this suggests that aldehyde groups are not required on the polymer to develop strength. Second, for PVAm/AParez systems at neutral pH, handsheet wet strength and dry strength both decrease as the concentration of AParez increases (codes 64, 65 and 66). Code 65 provides the highest tissue strength at the lowest polymer concentration; this suggests that the aldehyde functionalities of the AParez are involved in the synergetic strength increase.

**Example 8: Polyvinylamine/Carboxymethyl cellulose bicomponent strength agents - effect of polymer ratio**

A slurry of pulp fibers as described in Example 1 was prepared. A bicomponent strength system was formed in the slurry which included the following compounds:

- a carboxy methyl cellulose (CMC) (Mw 250,000 Daltons)
- 1% aqueous solution of a polyvinylamine (BASF Catiofast® PR 8106)



The degree of substitution for CMC was approximately 0.65 to 0.9. For this study, CMC was added first, followed by PVAm. The total polymer concentration was kept at 10 Kg/T of dry fiber. pH was held at 6.8. Handsheets were prepared as described in Example 1.

- 5 The effect of polymer ratio on the handsheet properties is presented in Table 8. At a constant polymer concentration of 10 Kg/T of dry fiber, adjusting the PVAm/CMC ratio affects each property of interest. Peak strength properties are attained at PVAm/CMC ratios between 5:1 and 2:1 (codes 72-73). This data illustrate that strength development does not necessarily require chemical interaction between amine (PVAm) and aldehyde (CParez®) functionalities.

10 **Table 8: PVAm/CMC Bicomponent Strength Agents - Effect of Polymer Ratio**  
(pH=6.8, 10-kg/T polymer concentration, CMC added first)

| Code    | PVAm:C<br>MC<br>Ratio | Dry TI<br>(Nm/g) | Wet TI<br>(Nm/g) | Wet TI<br>1-hr<br>(Nm/g) | %Wet TI<br>remain<br>after 1-hr | %<br>Wet/Dry<br>TI | %Peak<br>Stretch | TEA@<br>Peak<br>(J/m <sup>2</sup> ) | E<br>(kgf) |
|---------|-----------------------|------------------|------------------|--------------------------|---------------------------------|--------------------|------------------|-------------------------------------|------------|
| control | -                     | 10.16            | .79              | .61                      | 77                              | 8                  | .82              | 3.32                                | 338        |
| 71      | 1:0                   | 14.02            | 3.65             | 3.01                     | 82                              | 26                 | .92              | 5.13                                | 387        |
| 72      | 5:1                   | 19.99            | 6.2              | 5.17                     | 83                              | 31                 | 1.52             | 12.64                               | 416        |
| 73      | 2:1                   | 22.54            | 5.79             | 5.03                     | 87                              | 26                 | 1.64             | 15.26                               | 407        |
| 74      | 1:1                   | 19.69            | 3.84             | 2.88                     | 75                              | 20                 | 1.43             | 11.71                               | 465        |
| 75      | 1:2                   | 12.99            | 1.37             | 1.21                     | 88                              | 11                 | .93              | 4.82                                | 376        |
| 76      | 1:5                   | 10.90            | .72              | .66                      | 92                              | 7                  | .88              | 3.89                                | 342        |
| 77      | 0:1                   | 11.28            | .78              | .52                      | 66                              | 7                  | .78              | 3.44                                | 370        |

15 **Example 9: Polyvinylamine/Carboxymethyl cellulose bicomponent strength agents - effect of polymer order of addition**

A slurry of pulp fibers as described in Example 1 was prepared. A bicomponent strength system was formed in the slurry which included the following compounds:

- 20 a modest molecular weight (Mw 250,000 Daltons) carboxymethyl cellulose (CMC)
- 1% aqueous solution of a polyvinylamine (BASF Catiofast® PR 8106)

The components were at a 2:1 PVAm/CMC ratio. The degree of substitution for CMC was approximately 0.65 to 0.9. For this study, each polymer

served as the initial charge to the furnish. Moreover, a polyelectrolyte complex was prepared, at the defined ratio, for single charge application. The total polymer concentration was kept at 10 Kg/T of dry fiber. pH was held at 6.8. Handsheets were prepared as described in Example 1 and tested.

5 The effect of polymer order of addition on the handsheet properties is summarized in Table 9. The order of polymer addition significantly impacts handsheet properties. Best wet strength results are achieved with the sequential polymer addition and CMC added first.

10 **Table 9:** PVAm/CMC Bicomponent Strength Agents - Effect of order of Polymer addition (pH=6.8, 10-kg/T polymer concentration, PVAm/CMC ratio = 2/1)

| Code | Polymer added first | Dry TI (Nm/g) | Wet TI (Nm/g) | Wet TI 1-hr (Nm/g) | %Wet TI remain after 1-hr | % Wet/Dry TI | %Peak Stretch | TEA@ Peak (J/m <sup>2</sup> ) | E (kgf) |
|------|---------------------|---------------|---------------|--------------------|---------------------------|--------------|---------------|-------------------------------|---------|
| 78   | PVAm                | 20.83         | 4.81          | 3.75               | 78                        | 23           | 1.72          | 15.24                         | 483     |
| 79   | CMC                 | 21.76         | 5.69          | 4.54               | 80                        | 26           | 1.62          | 14.60                         | 505     |
| 80   | Complex             | 14.47         | 2.88          | 2.7                | 94                        | 20           | 1.05          | 6.03                          | 394     |

**Example 10: Polyvinylamine/Carboxy Methyl Cellulose bicomponent strength agents - effect of polymer concentration**

15 A slurry of pulp fibers as described in Example 1 was prepared except that . A bicomponent strength system was formed in the slurry which included the following compounds:

- a modest molecular weight (Mw 250,000 Daltons) carboxymethyl cellulose (CMC)
- aqueous solution of a polyvinylamine (BASF Catiofast® PR 8106)

20 The components were used in combination at a 2:1 PVAm/CMC ratio. The degree of substitution for CMC was approximately 0.65 to 0.9. For this study, the CMC component was added first to the furnish, the furnish was mixed for 10 minutes, and then the polyvinylamine was added to the furnish, and the furnish was mixed for an additional 2 minutes. pH was held at 6.8, and the total polymer concentration in the furnish was varied with the different codes. Handsheets were prepared as described in Example 1 and tested.

25

The effect of total polymer concentration on the handsheet properties is summarized in Table 10. Wet strength, dry strength, wet over dry strength ratio, toughness and rigidity increase as a function of total polymer concentration. Wet strength permanence, while independent of polymer concentration, mimics the response of Kymene®.

**Table 10: PVAm/CMC Bicomponent Strength Agents - Effect of Polymer concentration (pH=6.8, PVAm/CMC ratio = 2/1, CMC added first)**

| Code    | Polymer Concentration (mg/g) | Dry TI (Nm/g) | Wet TI (Nm/g) | Wet TI 1-hr (Nm/g) | %Wet TI remain after 1-hr | % Wet/Dry TI | %Peak Stretch | TEA@ Peak (J/m <sup>2</sup> ) | E (kgf) |
|---------|------------------------------|---------------|---------------|--------------------|---------------------------|--------------|---------------|-------------------------------|---------|
| control | 0                            | 10.14         | .85           | .69                | 81                        | 8            | .83           | 3.34                          | 338     |
| 81      | 2                            | 12.65         | 1.64          | 1.39               | 85                        | 13           | .87           | 4.42                          | 422     |
| 82      | 4                            | 15.43         | 3.10          | 2.58               | 83                        | 20           | 1.12          | 7.05                          | 440     |
| 83      | 6                            | 17.39         | 3.63          | 3.14               | 87                        | 21           | 1.33          | 9.80                          | 456     |
| 84      | 10                           | 22.54         | 5.79          | 5.03               | 86                        | 26           | 1.64          | 15.26                         | 407     |
| 85      | 15                           | 23.92         | 6.66          | 5.49               | 82                        | 28           | 1.64          | 16.16                         | 488     |

#### Example 11 – Chitosan/CParez® Bicomponent Strength Agents

A slurry of pulp fibers as described in Example 1 was prepared except that 50 g (oven-dry basis) of pulp fibers were soaked in 8 liters of deionized water for a fiber furnish used in the formation of the handsheets having a consistency of 0.625%. A bicomponent strength system was formed in the slurry which included the following compounds:

- Chitosan (a natural polysaccharide containing primary amine functionality)
- 1% aqueous solution of Parez 631NC (a cationic glyoxylated polyacrylamide) manufactured by Cytec Industries (CParez®)

The use of Chitosan as a dry and wet strength additive in papermaking is documented. The first component was added to the furnish, the furnish was mixed for 10 minutes, the second component was added to the furnish, and the furnish was then mixed an additional 2 minutes. pH was held at neutral. Handsheets were prepared as described in Example 1 and then tested. When added to the furnish in conjunction with glyoxylated polyacrylamides (cationic Parez 631NC) sheet characteristics similar to the polyvinylamine/cationic Parez system were obtained. That is, a synergistic strength affect dependent on order of

addition of the two materials. This would suggest that this effect is most likely to occur with any polymeric amine and aldehyde combination. The data for Chitosan and glyoxylated polyacrylamide sheets are shown in Table 11, below.

**Table 11 – Chitosan/Parez Strength System**

| Code | Parez (Kg/T) | Chitosan (Kg/T) | Dry TI (Nm/g) | % increase over control (Dry TI) | Wet TI (Nm/g) | % increase over control (Wet TI) |                                |
|------|--------------|-----------------|---------------|----------------------------------|---------------|----------------------------------|--------------------------------|
| 86   | 0            | 0               | 15.5          | 0%                               | 0.9           | 0%                               |                                |
| 87   | 5            | 0               | 19.9          | 29%                              | 3.2           | 239%                             |                                |
| 88   | 10           | 0               | 24.3          | 57%                              | 4.9           | 420%                             |                                |
| 89   | 0            | 5               | 15.6          | 1%                               | 1.5           | 59%                              |                                |
| 90   | 0            | 10              | 16.9          | 9%                               | 2.0           | 116%                             |                                |
| 91   | 5            | 5               | 19.1          | 23%                              | 3.3           | 252%                             | Chitosan added 1 <sup>st</sup> |
| 92   | 10           | 10              | 26.5          | 71%                              | 5.0           | 427%                             | Chitosan added 1 <sup>st</sup> |
| 93   | 5            | 5               | 27.2          | 76%                              | 5.4           | 476%                             | Parez added 1st                |
| 94   | 10           | 10              | 34.9          | 126%                             | 7.7           | 720%                             | Parez added 1st                |

5

It will be appreciated that the foregoing examples, given for purposes of illustration, are not to be construed as limiting the scope of this invention. Although only a few exemplary embodiments of this invention have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this invention which is defined in the following claims and all equivalents thereto. Further, it is recognized that many embodiments may be conceived that do not achieve all of the advantages of some embodiments, yet the absence of a particular advantage shall not be construed to necessarily mean that such an embodiment is outside the scope of the present invention.

10

15

**WHAT IS CLAIMED IS:**

1. A process for forming a paper web comprising:  
providing a slurry of pulp fibers;  
adding a first component comprising a polymer having at least about  
1.5 m-eq primary amine functionality per gram of polymer and a molecular weight  
5 of at least about 10,000 Daltons to the slurry of pulp fibers;  
adding a second component to the slurry of pulp fibers, the second  
component being selected from the group consisting of polymeric anionic  
compounds and polymeric aldehyde functional compounds, wherein the second  
component is added to the slurry of pulp fibers separately from the first  
10 component;  
depositing the slurry of pulp fibers containing the first and second  
components on a forming fabric; and  
drying the slurry of pulp fibers to form a paper web, wherein the first  
and second components form a bicomponent strengthening system in the paper  
15 web.
2. A process as defined in claim 1, wherein the first and second  
components form a polyelectrolyte complex in the slurry of pulp fibers.
3. A process as defined in claim 1, wherein the first and second  
components are bonded to each other in the bicomponent strengthening system.
4. A process as defined in claim 3, wherein the first and second  
components are capable of forming covalent bonds with each other.
5. A process as defined in claim 1, wherein the first component is a  
polyvinylamine.
6. A process as defined in claim 5, wherein the polyvinylamine  
comprises vinylformamide units, at least about 50% of which have been  
hydrolyzed to offer amine functionality.
7. A process as defined in claim 5, wherein the polyvinylamine  
comprises vinylformamide units, at least about 70% of which have been  
hydrolyzed to offer amine functionality.
8. A process as defined in claim 1, wherein the first component is a  
polysaccharide having primary amine functionality.

9. A process as defined in claim 1, wherein the first component is added to the slurry of pulp fibers before the second component.
10. A process as defined in claim 1, wherein the first component is added to the slurry of pulp fibers after the second component.
11. A process as defined in claim 1, wherein the second component comprises a cationic polymeric aldehyde functional compound.
12. A process as defined in claim 11, wherein the second component comprises a glyoxylated polyacrylamide.
13. A process as defined in claim 1, further comprising adjusting the pH of the slurry of pulp fibers to a pH of less than about 6.
14. A process as defined in claim 1, wherein the first component comprises at least about 11 m-eq primary amine per gram of the polymer.
15. A process as defined in claim 1, wherein the first component comprises at least about 15 m-eq primary amine per gram of the polymer.
16. A process as defined in claim 1, wherein the paper web has less than about 70% of the initial wet tensile index remaining after soaking in water for about one hour.
17. A process as defined in claim 1, wherein the paper web has more than about 70% of the initial wet tensile index remaining after soaking in water for about one hour.
18. A process as defined in claim 1, wherein the first and second components are added to the slurry of pulp fibers in a ratio of between about 5:1 to about 1:5.
19. A process as defined in claim 1, further comprising adjusting the pH of the slurry of pulp fibers to a pH greater than about 6.
20. A process as defined in claim 1, wherein the second component comprises a polymeric anionic compound having carboxy functionality.
21. A process as defined in claim 1, wherein the first component comprises a polymer having at least about 10 m-eq primary amine functionality per gram of polymer and a molecular weight of at least about 20,000 Daltons.
22. A bicomponent strengthening system for a paper web comprising a first component comprising a polymer having at least about 1.5 m-eq primary

amine functionality per gram of polymer and a molecular weight of at least about 10,000 Daltons and a second component selected from the group consisting of polymeric anionic compounds and polymeric aldehyde functional compounds, wherein the bicomponent strengthening system develops in a slurry of pulp fibers  
5 after the first component and the second component are sequentially added to the slurry.

23. A bicomponent strengthening system as defined in claim 22, wherein the first component comprises a polyvinylamine.

24. A bicomponent strengthening system as defined in claim 22, wherein the first component comprises a polysaccharide having primary amine functionality.

25. A bicomponent strengthening system as defined in claim 22, wherein the first component is added to the slurry of pulp fibers before the second component.

26. A bicomponent strengthening system as defined in claim 22, wherein the first component is added to the slurry of pulp fibers after the second component.

27. A bicomponent strengthening system as defined in claim 22, wherein the second component comprises a cationic polymeric aldehyde functional compound.

28. A bicomponent strengthening system as defined in claim 27, wherein the second component comprises a glyoxylated polyacrylamide.

29. A bicomponent strengthening system as defined in claim 22, wherein the bicomponent strengthening system develops in the slurry of pulp fibers at a pH less than about 6.

30. A bicomponent strengthening system as defined in claim 22, wherein the first and second components form a polyelectrolyte complex in the slurry of pulp fibers.

31. A bicomponent strengthening system as defined in claim 22, wherein the first and second components are bonded to each other.

32. A bicomponent strengthening system as defined in claim 31, wherein the first and second components are capable of forming covalent bonds with each other.

33. A bicomponent strengthening system as defined in claim 22, wherein the first component has greater than about 11 m-eq primary amine per gram of polymer.

34. A bicomponent strengthening system as defined in claim 22, wherein the first component has greater than about 15 m-eq primary amine per gram of polymer.

35. A bicomponent strengthening system as defined in claim 22, comprising the first and second components in a ratio to each other of between about 5:1 and about 1:5.

36. A bicomponent strengthening system as defined in claim 22, wherein second component comprises a polymeric anionic compound having carboxy functionality.

37. A bicomponent strengthening system as defined in claim 22, wherein the second component comprises carboxymethyl cellulose.

38. A bicomponent strengthening system as defined in claim 22, wherein the bicomponent strengthening system develops in the slurry of pulp fibers at a pH greater than about 6.

39. A bicomponent strengthening system as defined in claim 22, wherein the bicomponent strengthening system provides temporary wet strength to the paper web.

40. A bicomponent strengthening system as defined in claim 22, wherein the bicomponent strengthening system provides permanent wet strength to the paper web.

41. A bicomponent strengthening system as defined in claim 22, wherein the first component comprises a polymer having at least about 10 m-eq primary amine functionality per gram of polymer and a molecular weight of at least about 20,000 Daltons.



42. A bicomponent strengthening system as defined in claim 22, wherein the first component comprises a polyvinylamine polymer comprising partially hydrolyzed polyvinylformamide.

43. A bicomponent strengthening system as defined in claim 42, wherein the degree of hydrolyzation of the polyvinylformamide is about 50% or greater.

44. A bicomponent strengthening system as defined in claim 42, wherein the degree of hydrolyzation of the polyvinylformamide is about 70% or greater.

45. A bicomponent strengthening system as defined in claim 42, wherein the degree of hydrolyzation of the polyvinylformamide is about 90% or greater.

46. A method for decreasing the amount of low molecular weight organic chlorinated compounds in the waste stream of a paper manufacturing process comprising:

- 5 providing a paper manufacturing process, wherein said paper manufacturing process comprises the formation of a slurry of pulp fibers and the addition of a chlorinated strengthening agent to a paper;
- eliminating the addition of said chlorinated strengthening agent from the paper manufacturing process;
- adding a first component comprising a polymer having at least about 10 1.5 m-eq primary amine functionality per gram of polymer and a molecular weight of at least about 10,000 Daltons to the slurry of pulp fibers;
- adding a second component to the slurry of pulp fibers, the second component being selected from the group consisting of polymeric anionic compounds and polymeric aldehyde functional compounds wherein the second 15 component is added to the slurry of pulp fibers separately from the first component;
- depositing the slurry of pulp fibers containing the first and second components on a forming fabric; and
- drying the slurry of pulp fibers to form a paper web, wherein the first 20 and second components form a bicomponent strengthening system which replaces the chlorinated strengthening agent in the paper web.

47. A method as defined in claim 46, wherein the chlorinated strengthening agent comprises a polyamide-epichlorohydrin strengthening agent.

48. A method as defined in claim 46, wherein the first component comprises a polyvinylamine.

49. A process as defined in claim 48, wherein the polyvinylamine has at least about 50 mole% vinylamine per gram of polyvinylamine.

50. A process as defined in claim 48, wherein the polyvinylamine has at least about 70 mole% vinylamine per gram of polyvinylamine.

51. A method as defined in claim 46, wherein the first component comprises a polysaccharide having primary amine functionality.

52. A method as defined in claim 46, wherein the first component is added to the slurry of pulp fibers before the second component.

53. A method as defined in claim 46, wherein the first component is added to the slurry of pulp fibers after the second component.

54. A method as defined in claim 46, wherein the second component is a cationic polymeric aldehyde functional compound.

55. A method as defined in claim 54, wherein the second component is a glyoxylated polyacrylamide.

56. A method as defined in claim 46, further comprising adjusting the pH of the slurry of pulp fibers to a pH less than about 6.

57. A method as defined in claim 46, further comprising adjusting the pH of the slurry of pulp fibers to a pH greater than about 6.

58. A method as defined in claim 46, wherein the first component has greater than about 11 m-eq primary amine per gram of polymer

59. A method as defined in claim 46, wherein the first component has greater than about 15 m-eq primary amine per gram of polymer.

60. A method as defined in claim 46, wherein the first and second components are added to the slurry of pulp fibers in a ratio of between about 5:1 to about 1:5.

61. A method as defined in claim 46, wherein the second component comprises a polymeric anionic compound having carboxy functionality.

62. A paper product comprising:  
a paper web formed from a slurry of papermaking fibers; and

a bicomponent strengthening system comprising a first component comprising a polymer having at least about 1.5 m-eq primary amine functionality per gram of polymer and a molecular weight of at least about 10,000 Daltons and a second component selected from the group consisting of polymeric anionic compounds and polymeric aldehyde functional compounds, wherein the first  
5 component and the second component are sequentially added to the slurry of papermaking fibers.

63. The paper product of claim 62, wherein the paper web has a bulk greater than about 2 cc/g.

64. The paper product of claim 62, wherein the first component comprises a polymer having at least about 10 m-eq primary amine functionality per gram of polymer and a molecular weight of at least about 20,000 Daltons.

65. The paper product of claim 62, wherein the paper web has less than about 70% of the initial wet tensile index remaining after soaking in water for about one hour.

66. The paper product of claim 65, wherein the paper web has a dry tensile index greater than about 22 Nm/g.

67. The paper product of claim 65, wherein the paper web has a dry tensile index greater than about 25 Nm/g.

68. The paper product of claim 65, wherein the paper web has a wet tensile index less than about 2 Nm/g after soaking in water for about one hour.

69. The paper product of claim 65, wherein the paper web has less than about 60% of the initial wet tensile index remaining after soaking in water for about one hour.

70. The paper product of claim 62, wherein the paper web has more than about 70% of the initial wet tensile index remaining after soaking in water for about one hour, wherein the paper web does not comprise any polyamine epichlorohydrin strengthening agents.

71. The paper product of claim 70, wherein the paper web has a dry tensile index greater than about 20 Nm/g.

72. The paper product of claim 71, wherein the paper web has a dry tensile index greater than about 25 Nm/g.

73. The paper product of claim 70, wherein the paper web has more than about 80% of the initial wet tensile index remaining after soaking in water for about one hour.

74. The paper product of claim 62, wherein the first component comprises a polyvinylamine.

75. The paper product of claim 62, wherein the first component comprises a polysaccharide having primary amine functionality.

76. The paper product of claim 62, wherein the second component comprises a cationic polymeric aldehyde functional compound

77. The paper product of claim 76, wherein the second component comprises a glyoxylated polyacrylamide.

78. The paper product of claim 62, wherein the second component comprises a polymeric anionic compound having carboxy functionality.

79. The paper product of claim 62, wherein the second component comprises carboxymethyl cellulose.

80. The paper product of claim 62, wherein the paper product has a bulk greater than about 5 cc/g.

81. The paper product of claim 62, wherein the paper product has a basis weight between about 5 and about 200 gsm.

82. The paper product of claim 62, wherein the paper product comprises a multi-layered paper web, wherein the bicomponent strengthening system is added to one or more layers of the paper web.

83. The paper product of claim 82, wherein the multi-layered paper web comprises a layer comprising soft wood pulp and a layer comprising hard wood pulp, wherein the bicomponent strengthening system is added to the layer comprising soft wood pulp.

1/1

| Product name | Product name Current | Product name New | KW    | pH      | Charge density | Molar mass.            | Deg. Of Hydrolysis | Viscosity (mPas) | Solids (%) |
|--------------|----------------------|------------------|-------|---------|----------------|------------------------|--------------------|------------------|------------|
| Catiofast    | PR 8106              | VFH              | 85-90 | 7.0-9.0 | 21             | appr. g/mol<br>400 000 | percent<br>90      | 500-2500         | 20-22      |
| Catiofast    | PR 8085              | VMP              | 85-90 | 6.5-7.5 | 7              | 400 000                | 30                 | 500-2500         | 15-17      |
| Catiofast    | PR 8087              | VSH              | 85-90 | 6.5-7.5 | 11             | 400 000                | 50                 | 500-2500         | 17-19      |
| Catiofast    | PR8104               |                  | 85-90 | 7.0-9.0 | 2.3            | 400 000                | 10                 | 500-2500         | 13-15      |
| Catiofast    | PR8102               |                  | 85-90 | 6.5-7.5 | 17             | 400 000                | 75                 | 500-2500         | 19-21      |

Figure 1

# INTERNATIONAL SEARCH REPORT

National Application No  
PCT/US 03/32848

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 D21H23/04 D21H17/71 D21H17/20 D21H17/37 D21H17/42  
D21H17/56

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category * | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No.       |
|------------|--|-----------------------------|
| A          | WO 97/30118 A (CALLAWAY CORP)<br>21 August 1997 (1997-08-21)<br><br>the whole document   | 1,12,22,<br>28,46,<br>62,77 |
| A          | PATENT ABSTRACTS OF JAPAN<br>vol. 2002, no. 02,<br>2 April 2002 (2002-04-02)<br>& JP 2001 295193 A (KURITA WATER IND<br>LTD;MITSUI CYTEC KK),<br>26 October 2001 (2001-10-26)<br>abstract<br><br>-----<br>-/-- | 1,22,46,<br>62              |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

30 April 2004

Date of mailing of the international search report

11/05/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Naeslund, P

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 03/32848

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT |   |                                 |
|--|---|---------------------------------|
| Category *   | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.           |
| A  | PATENT ABSTRACTS OF JAPAN<br>vol. 1996, no. 05,<br>31 May 1996 (1996-05-31)<br>& JP 08 027693 A (MITSUBISHI PAPER MILLS LTD), 30 January 1996 (1996-01-30)<br>abstract<br>--- | 1, 22, 46,<br>62                |
| A  | PATENT ABSTRACTS OF JAPAN<br>vol. 1999, no. 10,<br>31 August 1999 (1999-08-31)<br>& JP 11 140787 A (TOKIWA:KK),<br>25 May 1999 (1999-05-25)<br>abstract<br>---                | 62                              |
| A  | FR 2 682 132 A (ZSCHIMMER SCHWARZ FRANCE)<br>9 April 1993 (1993-04-09)<br><br>abstract<br>---   | 1, 12, 22,<br>28, 46,<br>62, 77 |
| A  | US 4 210 489 A (MARKOFKY SHELDON B)<br>1 July 1980 (1980-07-01)<br>cited in the application<br>the whole document<br>---  | 1-83                            |
| A  | EP 0 289 823 A (AMERICAN CYANAMID CO)<br>9 November 1988 (1988-11-09)<br>the whole document<br>-----  | 1-83                            |

1

Form PCT/ISA/210 (continuation of second sheet) (January 2004)

page 2 of 2

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/32848

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s)                                  | Publication<br>date                                  |
|---|---|---------------------|---|--|
| WO 9730118                                | A | 21-08-1997          | AU 1956597 A<br>ID 18934 A<br>WO 9730118 A1<br>ZA 9701186 A | 02-09-1997<br>20-05-1998<br>21-08-1997<br>25-08-1997 |
| JP 2001295193                             | A | 26-10-2001          | NONE  |  |
| JP 08027693 3                             | A |                     | NONE  |  |
| JP 11140787 3                             | A |                     | NONE  |  |
| FR 2682132                                | A | 09-04-1993          | FR 2682132 A1   | 09-04-1993   |
| US 4210489                                | A | 01-07-1980          | NONE  |  |
| EP 0289823                                | A | 09-11-1988          | EP 0289823 A2<br>FI 882076 A<br>JP 63288296 A               | 09-11-1988<br>06-11-1988<br>25-11-1988               |

Form PCT/ISA/210 (patent family annex) (January 2004)